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THE

PHYSICAL REVIEW

ARTHUR GORDON WEBSTER

1864–1923

The sudden death of Professor Webster of Clark University on the fifteenth of May, at Worcester, was a great shock to all who knew him. It is indeed astonishing that a man of such attainments should wish to end such a distinguished life when his health and mental powers were unimpaired.

The members of the American Physical Society are under a very particular obligation to him. It was he who took the leading part in the founding of the Society in 1899; he succeeded Rowland and Michelson as our third president during 1903 and 1904; and at our meetings his extemporaneous comments, penetrating, often humorous, and always admirably expressed, will be greatly missed now that his eloquent voice is silent.

Endowed with a clear, quick mind, a remarkable memory, a gift for languages, self-assurance, and unusual physical vigor, and given by his early training a broad cultural background, he was clearly destined for a distinguished career. In 1885, he was graduated from Harvard with honor. After studying at Paris, at Stockholm, and then under Kundt and Helmholtz, he received a doctor's degree from the University of Berlin in 1890. On his return to this country he was offered a professorship at Amherst, but decided to go to the newly founded graduate university where he remained until his death. The Elihu Thomson prize was awarded to him in 1895. He was honored with degrees by Tufts (1905), Hobart (1908), and Princeton (1922). The Lowell Institute, the University of Pennsylvania, Columbia, and the Royal Institution of London invited him to give series of lectures. He was elected to membership in many of the most distinguished scientific societies of the world. Few American physicists have been as widely known and honored.

His ability as an experimental physicist was demonstrated by his measurement of the period of electrical oscillations by means of a drop chronograph, the research for which he received the Elihu Thomson prize; by the measurements of the intensity of sound made with the phonometer he developed; and by the more recent experiments dealing with ballistics. Yet by temperament and natural endowment, he was pre-eminently a scholar. He read constantly, apprehended quickly, remembered accurately, and as a result his information was unusually wide and thorough. He enjoyed teaching and lecturing, for he did both well; and his most valuable and permanent contributions to physics are undoubtedly his beautifully clear and systematic treatises on mechanics, on electricity and magnetism, and on the partial differential equations of physics (not yet published).

In attacking policies of which he disapproved, he was vigorous, outspoken, and astonishingly guileless; but in judging individuals, he was always kind and generous. His students, tragically few because of his unfortunate isolation, always found him most sympathetic and encouraging. In fact, in spite of his tendency to sarcasm in public addresses, he was a man of singularly open and kindly disposition. By his untimely death, the world has lost a great scholar, and many of us a loyal and warm-hearted friend.—*G. S. F.*

SHORT ELECTRIC WAVES

By E. F. Nichols and J. D. Tear

Abstract

Extension of electric wave spectrum to wave-length of 1.8 mm.—As a result of improved apparatus and technique, the electric wave spectrum has recently been extended two octaves nearer to the long wave limit of the heat spectrum. *Improved Hertzian oscillators* were made with pairs of tungsten cylinders 0.5 to 0.2 mm in diameter and 5 to 0.2 mm long, sealed into glass. Increased efficiency was obtained by use of jets of compressed air for the auxiliary gaps and of kerosene for the main gap. As the length of oscillator decreases from 10 to 0.4 mm, the ratio of fundamental wave-length to oscillator length increases from 2.7 to 4.8, making progress increasingly difficult. To measure the radiation, various *improved radiometer receivers* were developed. Receiving elements either of short lengths of 1 μ platinum wire or of narrow strips of platinum film deposited on thin mica were substituted for the usual black vanes. The sensitive systems were suspended by quartz fibers and weighed only $\frac{1}{2}$ to 1 mg. By proper choice and adjustment of the elements, the receiver can be made either selective or not. By direct test, the deflection was proved proportional to the incident energy. Mirrors and paraffin lenses were used in focussing the energy from the oscillator on the receiving element. *Wave-length measurements* were made with the aid of a Boltzmann divided mirror interferometer, and *energy-distribution curves* were obtained for various oscillators and receivers. To correct for the variations in the emission of the oscillator, readings were made, simultaneously, of the total emission with a check receiver, and of the radiation of a particular wave-length. On account of the high damping of the oscillator, the curves obtained show the predominant influence of the fundamental frequency of the receiver but also maxima when partials of the oscillator coincide with one or other of the partials of the receiver. The shortest fundamental wave-length obtained is 1.8 mm, two octaves shorter than the shortest previously measured, 7 mm. An upper partial of 0.8 mm was also observed. Greater homogeneity was secured by use of a *reflecting echelon*, $\frac{1}{2}\lambda$ between treads, since it reflects selectively. A simple mounting permitting easy adjustment is described. Two such echelons with steps at right angles give, under suitable conditions, a fair approximation to monochromatic radiation. By use of such echelons it should be possible to isolate upper partials still shorter than those so far measured.

THERE is doubtless little need of any further experimental proof of the essential identity between heat waves and electric waves, yet for the sake of completeness, further effort to bridge the existing gap between these two spectra seems warranted. Moreover, the optical properties of many substances, of which water is a notable example, undergo such unusual changes in crossing this unknown region as to lend some theoretical importance to its further exploration.

An interval of more than 15 octaves separated the highest frequency of Hertz's shortest electric waves from the frequency of Langley's longest heat waves. By the experiments of Righi,[1] Lebedew,[2] Lampa,[3] and Möbius [4] on the one side and by those of Rubens with Nichols,[5] Wood,[6] and Von Baeyer [7] on the other, this unexplored interval had been progressively reduced to 4 or 5 octaves.

The precise extent of the conquered territory on the electric wave side is less certain and definite than the outer known limits of the heat spectrum. The difficulties which beset the explorer in the two fields differ in many details but agree in one most important respect. Further progress in both domains awaits the development of more sensitive and dependable receiving apparatus. However, the apparatus and technique of short electric wave experiments has been less extensively, methodically, and painstakingly developed than the instruments and methods employed in the infra-red spectrum. For this reason, if for no other, an attack on the problem of bringing the two spectra together seems more promising if made on the electric wave side.

The experiments described in this paper were undertaken, therefore, in the hope that by devising better instruments and better and more accurate methods of experimentation with short electric waves, further progress might be made in narrowing the still unexplored region between the two spectra and in making the results of future short electric wave experiments more strictly quantitative and trustworthy.

Source of Radiation

A very small Hertz doublet immersed in kerosene was used as a source. To adapt this form of oscillator to short wave emission a number of departures from earlier practice were made. Instead of using small cylinders of platinum for the two halves of the doublet, cylinders of tungsten were substituted and found in use to wear away more evenly and less rapidly than platinum.

For the different oscillators employed in the present experiments, tungsten cylinders, varying in length from several millimeters to 0.2 mm and in diameter from 0.5 mm to 0.2 mm, were sealed into the closed ends of tubes of hard glass having the same expansion coefficient as the

[1] Righi, Mem. del R. Acad. dei Sc. del Inst. di Bologna, v. 4, 1894.

[2] Lebedew, Wied. Ann. 56, 1, 1895.

[3] Lampa, Wiener Ber. 105, 587 and 1049, 1896; 104, 1179, 1895.

[4] Möbius, Ann. der Phys. 62, 293, 1920.

[5] H. Rubens and E. F. Nichols, Phys. Rev. 4, 314, 1897; 5, 98 and 152, 1897; Ann. der Phys. 60, 418, 1897.

[6] H. Rubens and R. W. Wood, Phil. Mag. 21, 249, 1911.

[7] H. Rubens and O. Von Baeyer, Phil. Mag. 21, 689, 1911.

metal. These tubes T and T_1 were mounted, as shown in Fig. 1, in a holder A, hinged at H. The length of the spark gap between the tungsten cylinders c and c_1 was of the order of 0.01 mm and was adjustable to the

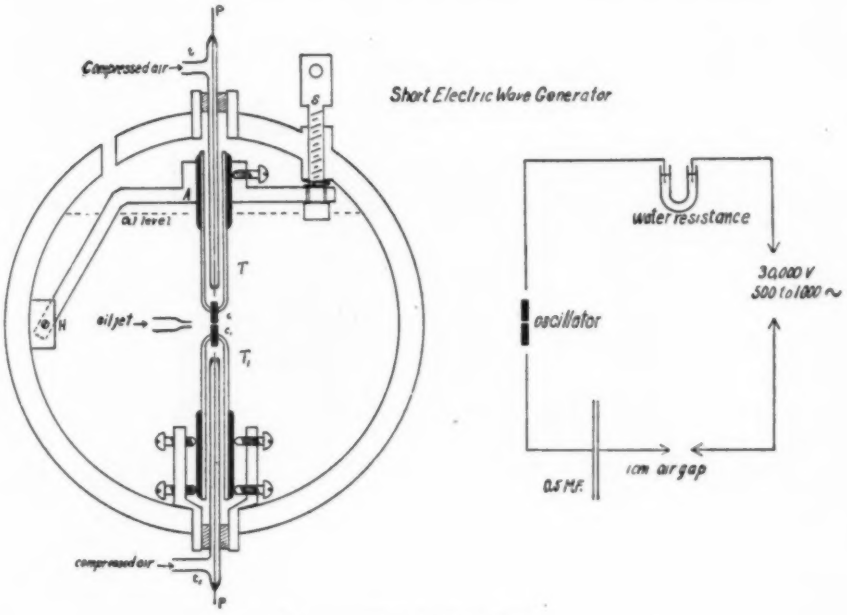

Fig. 1. Sketch of oscillator.

requisite precision by the micrometer screw S. In the open ends of the tubes T and T_1, inner tubes t and t_1 were introduced carrying wires from the high potential circuit P. The inner ends of these wires were brought near the outer ends of the tungsten doublet and separated from them only by short spark gaps in air. Side openings in the inner tubes admitted a stream of compressed air which served a threefold purpose. It more quickly de-ionized the air gaps after each discharge; it cooled the tungsten glass seals; and by a slight excess of pressure, it prevented kerosene from leaking into the air gaps through any imperfections in the tungsten glass seals.

The doublet was mounted at the center of curvature of a concave spherical mirror in a cylindrical brass case containing kerosene (see Fig. 2). The radiation issued through a circular mica-covered window, 4 cm in diameter, in the front of the oscillator box, and was formed into a parallel beam by a double convex paraffin lens.

As the intensity of radiation from the oscillator depends on the effective frequency of excitation which in turn is limited by the time required to restore the oil insulation in the main spark gap after each discharge, two methods were tried for shortening this period.

First, a kerosene jet from a centrifugal pump driven by an air turbine was directed toward the spark gap to hasten the clearing away of gas bubbles formed by the spark. The jet nozzle is indicated in Fig. 1, and the air turbine is seen at the left on top of the oscillator box in Fig. 2. Although with the jet in operation it is possible to increase the effective frequency of discharge by about fifty per cent, recourse to it has proved necessary only when the smallest oscillators were used.

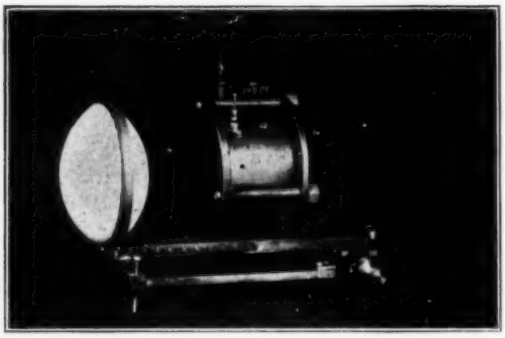

Fig. 2. Photo of oscillator.

Second, the kerosene in the oscillator case was put under pressure varying from 0.1 to 4 atmospheres. Intensity of radiation increased rapidly with pressure from 0.1 to 1 atmosphere and from there on more slowly, reaching a maximum at about 3 atmospheres, at which pressure an increase in intensity of about fifty per cent over that at one atmosphere was observed. The maximum at 3 atmospheres is probably an individual characteristic of the apparatus used, for beyond this pressure the available potential proved insufficient to break down the kerosene insulation at the spark gap for every excitation of the coil, hence the action became somewhat irregular. Although increased pressure thus gives a second means of increasing radiant intensity, the oscillator, for greater convenience, has ordinarily been operated at atmospheric pressure.

In addition to the oscillator, the high potential circuit included the secondary of an induction coil giving 30,000 volts, a water resistance, a spark gap, and a condenser, all in series. The primary circuit of the induction coil included a rotating mechanical make-and-break from which any frequency of interruption up to 1000 per second was readily obtained. The primary circuit also included an automatic time switch permitting the operation of the coil for any chosen time interval, thus affording a convenient means of accurately controlling the "exposure times" used in making observations.

The Receiver

The possibility of developing different types of metallic systems suspended by quartz fibers, as new forms of sensitive electric wave receivers, has been discussed elsewhere by one of the present writers.[8] Of this class, the radiometer type of receiver has been most worked on. This form was first mentioned by Hull who mounted a radiometer vane facing a high resistance section in the middle of a linear receiving resonator. Deflections of the radiometer vane were produced by the heat generated in the resonator resistance by electric oscillations.

Later Webb [9] mounted a linear resonator like Hull's, directly on a radiometer suspension. To make the radiometric impulse unilateral, a thin mica shield was mounted behind the high resistance portion of the resonator. Webb also mounted uniform strips of the thinnest obtainable metal foils, shielded on one side by mica, as radiometer vanes.

Webb's experiments served as the point of departure in designing a radiometric receiver for the present work. In changing from metal foils to light deposits of platinum on the thinnest mica, a marked increase in sensitiveness was obtained, and still further and more striking increases followed the substitution of mounted strands of platinum wire of the order of 1 μ in diameter. In all thermal electric wave receivers, the same problem is met. If the resistance is too high, the radiation sweeps past it; if too low, the radiation is almost wholly reflected or re-emitted. In neither case is the maximum energy absorbed. The best absorption resistances so far obtained have been reached through carefully controlled, cut and try experiments.

The forms of radiometer vanes tested in the present experiments have been various, but the methods of vane shielding and mounting have been similar. A typical suspension is shown at *a*, Fig. 3, in which the rotation axis *q*, a straight, fine-drawn rod of quartz or hard glass about 5 cm long and from 0.05 to 0.02 mm in diameter, hangs by a quartz fiber *f*. A silvered mirror *m* of microscope cover glass, 0.5 to 1 mm high by 1 mm wide and about .07 mm thick, is attached to *q*, to which the fine-drawn glass cross arms c_1 and c_2, carrying thin mica shields v_1 and v_2, (0.2 × 1) to (0.5 × 10) mm, are also made fast. The distance between the outside edges of v_1 and v_2 varied from 1 to 2 mm in different suspensions. Just in front of, but not touching v_1, and just behind, but not touching v_2, were mounted the various resonator heating elements. When these are warmed by absorption of electric radiation, the moments of the radiometric forces on both vanes lie in the same direction.

[8] E. F. Nichols, International Electrical Congress, St. Louis, 1904.

[9] H. W. Webb, Phys. Rev. **30**, 192, 1910.

All joints shown in Fig. 3 were made with minute bits of fused shellac, and the total weight of each of the various types of suspension was less than a milligram, and in some instances not more than one half milligram. It was by thus scaling down the linear dimensions and weight of the present suspension beyond those of earlier radiometers that the greater part of the greatly increased sensitivity was obtained.

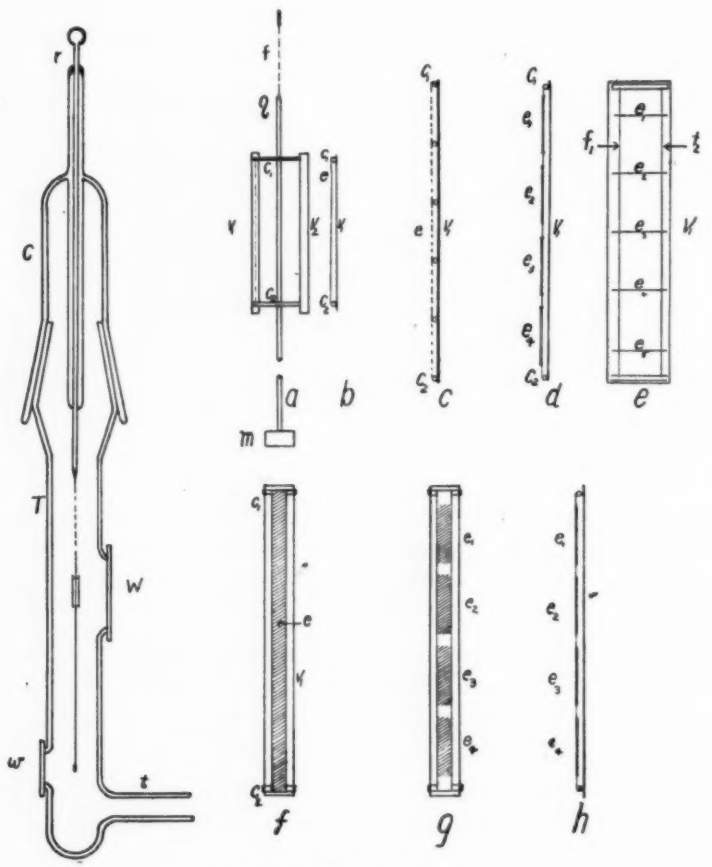

Fig. 3. Receiver types.

During tests, suspensions were mounted axially in a glass tube T, Fig. 3. The best working conditions were met by a tube of about 15 mm diameter. In such a housing, the mica walls, often set opposite radiometer vanes to increase the sensitiveness, are unnecessary. The tube T bears a ground joint at the top fitted by a cap C carrying a drawn down axial rod r to which the upper end of the quartz fiber f, bearing the suspension, is attached. By turning the cap C on the ground joint, the

orientation of the suspension can be varied at will. T has two side window openings W and w. The former, covered by an ebonite plate, admits the beam of electric waves; the latter is covered by plate glass, and through it the deflections of the suspended system were read with telescope and scale. A side tube t connects the receiver to a mercury pump. The receivers showed maximum sensitiveness for gas pressures of approximately .05 mm of mercury. In pumping out the receiver a black vaned torsion radiometer included in the same vacuum line and deflected by the rays from a constant tungsten lamp, was used as a rough pressure gauge. Deflections of this auxiliary radiometer were indicated by a light spot projected on a scale, and pumping was stopped when the radiometer deflection reached a maximum and turned back.

To guard against disturbances arising from stray radiation or other temperature differences, the receiver case was surrounded by cotton and packed in a thick-walled brass tube provided with the necessary window openings.

The resonator heating elements so far tried as receiver vanes fall into two general classes, (1) those made of fine Wollaston wire of about 1 μ diameter, and (2) those made by depositing light metal coatings on thin mica strips or quartz fibers by the method of evaporation or cathode discharge at low pressures.

Fig. 3*b* shows an enlarged receiver vane, edge on. The heater element e, of platinum wire 1 μ in diameter, is stretched between the cross rods c_1, c_2 in front of the thin mica shield v_1. This resonator had a fundamental period corresponding to its total length, and a complete series of upper partials.

The vane in Fig. 3*c* is similar in type to that in Fig. 3*b* except for a number of short glass rods used as bridges between c_1 and c_2. Over these bridges a continuous length of 1 μ wire could be stretched or a series of short discontinuous lengths reaching only from one bridge to the next. In the first instance, a fundamental was obtained similar to that for Fig. 3*b*, but with an accented upper partial of a frequency dependent upon the distance between bridges and also upon the added capacities thus introduced. For the discontinuous lengths, the fundamental corresponding to the total vane length disappeared altogether, of course, leaving a receiver tuned to the shorter wave-length.

In the arrangement of Fig. 3*d*, a quartz fiber is stretched between the cross arms c_1, c_2 in front of the shield v_1. To this fiber, short lengths of 1 μ wire e_1, e_2, e_3, etc., are attached. For the same dimensions, this receiver corresponds to a shorter wave-length resonance than the receiver 3*c*, because of smaller end capacities, and it is also more sharply selective because less damped.

In Fig. 3*e*, the receiver vane is shown face on. Two quartz fibers f_1, f_2 are stretched in front of the mica shield v_1, and short sections of 1 μ wire e_1, e_2, e_3, etc., are stretched from one fiber across to the other like the rungs of a ladder. This is the only receiver used in which the electric vector is horizontal instead of vertical.

Receiver vanes of the second class with resonator heating elements made of light metallic deposits were of the three principal forms shown in Figs. 3*f*, 3*g*, and 3*h*. In Fig. 3*f* a long, narrow, uniformly coated platinized strip *e* of very thin mica was attached to the cross rods c_1, c_2 in front of the mica shield v_1. In natural frequency and general characteristics, this mounting is comparable with that shown in Fig. 3*b*. Fig. 3*g* shows a variation from Fig. 3*f* produced by placing small bars across the thin mica strip while the metal coating was being deposited. The shadows of the bars divide the strip into rectangular fields e_1, e_2, e_3, etc. The resonance frequencies of these elements were often erratic, due probably to the fact that the shadowed spaces, though clear in appearance, were not invariably non-conducting. The results showed resonance frequencies corresponding to the dimensions of the individual fields, and additional lower frequencies corresponding probably to several fields acting as one. A variant on this type of resonance heater was constructed by cutting a uniform strip such as *e*, Fig. 3*f*, into short lengths and attaching these separately to another mica sheet. The frequencies thus obtained corresponded to the dimensions of the metal-coated rectangles, and there was no response to longer waves.

The vane shown in Fig. 3*h* has heater elements e_1, e_2, e_3, etc., made by depositing regional metal coatings on a quartz fiber. If care is taken in the process to effectively shield the quartz fiber between metallized sections and thus secure adequate insulation, results comparable to those with the heater elements e_1, e_2, e_3, etc., in Fig. 3*d* can be obtained.

When a receiver is first assembled, the suspension takes up some position usually quite independent of the position of the torsion cap. The introduction of a small quantity of radioactive material hastens the dissipation of any accidental static charges responsible for such disturbances so that after a brief interval the suspension readily responds to the torsion cap even with the finest fibers. In the present experiments the writers are indebted to Professor A. Kovarik of Yale, who very kindly supplied several polonium deposits on copper disks, which were placed in the various receivers; and later Dr. E. Karrer of the Applied Science Laboratory, National Lamp Works, kindly loaned some small tubes of radioactive material for the same use. A fiber was usually chosen which after a deflection brought the system back to zero in about twenty

seconds. For exposures of from one fifth to one and a half seconds the size of the deflections obtained depends but little on the torsion of the fiber and almost wholly upon the work done by the system against viscosity in moving through the residual gas.

To test the strict proportionality of receiver deflections to incident energy for this new type of electric wave receiver, the following experiment based on the polarizing action of wire gratings for electric waves was tried. The oscillator emitting a plane polarized beam was set with electric vector vertical. A receiver with vertical resonators of the type shown in Fig. 3*b* was placed in the beam from the oscillator. When a wire grating, with grating space small compared to the wave-length of

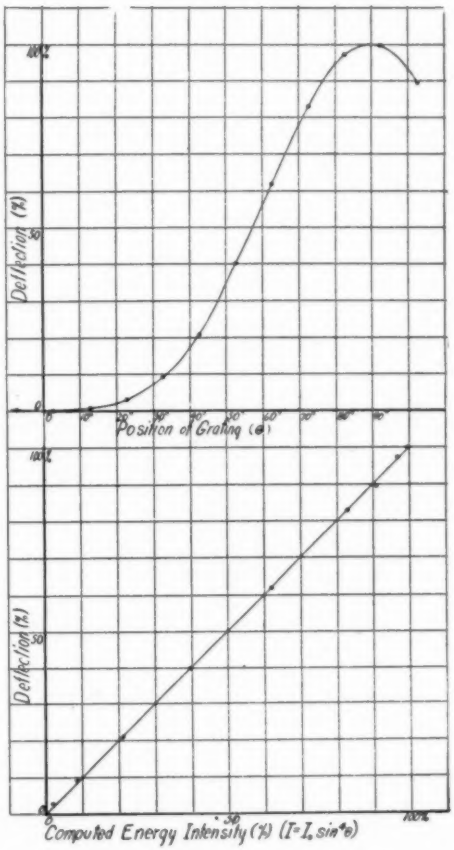

Fig. 4. Polarizing grating data.

the incident radiation, is placed between oscillator and receiver and rotated in a plane perpendicular to the line joining them, its polarizing action is, like that of a nicol introduced between polarizer and analyzer,

set parallel. By analogy, therefore, in our arrangement of oscillator, grating, and receiver, the grating transmission in different orientations should equal the product of incident energy by the fourth power of the sine of the angle between the direction of the grating wires and the vertical. For a wave-length of 18 mm and a grating of brass wires, 0.1 mm in diameter and spaced 32 to the centimeter, observed deflections and computed transmissions were proportional to within one per cent as will be seen from Fig. 4.

Wave-Length Measurements

The resonance absorption of all the various receiving elements tested was strongly selective and usually showed a pronounced absorption for a fundamental frequency and a diminishing selective absorption for a complete series of upper partials. The fundamental absorption wave-lengths of the different receivers employed ranged from 4 to 30 mm.

When oscillator and receiver are approximately in resonance, quite satisfactory wave-length measurements can be made with the familiar Boltzmann divided mirrors. A photograph of the Boltzmann interferometer employed is shown in Fig. 5. The mirror plates are of brass

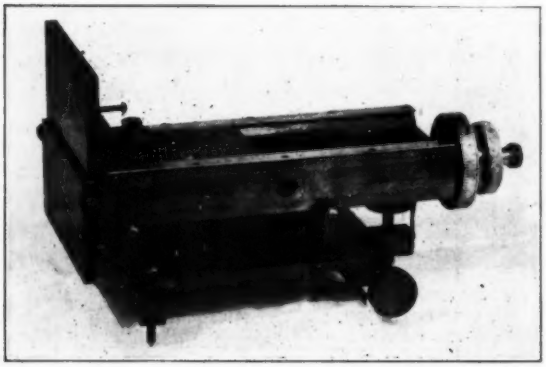

Fig. 5. Photo of Boltzmann interferometer.

($5 \times 10 \times 0.6$ cm), with plane surfaces. The lower half mirror is stationary; the upper half, mounted on a micrometer-screw slide, can be moved measured distances backward or forward. The mirror planes can be set accurately parallel by means of slow motion adjustments. Either mirror can also be turned about a vertical axis to deflect its beam to one side and again swung back to parallelism without loss of adjustment, thus making it easy at any time to test the energy equality of the two beams.

In Fig. 6 a diagram is shown of the arrangement of apparatus for

wave-length measurements. The oscillator at G is at the center of curvature of a spherical mirror m and in the principal focus of a double convex paraffin lens L_1. L_2 and L_3 denote equal paraffin lenses of 12 cm diameter and 8 cm focal length. A plane mirror is placed at A, the

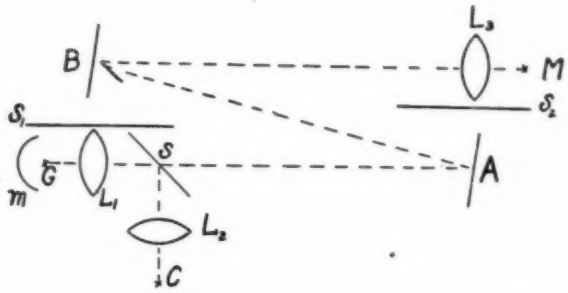

Fig. 6. Diagram for wave-length measurements.

interferometer at B, and the main receiver in the principal focus of L_3 at M. A portion of the energy of the parallel beam from the oscillator is reflected by a sheet of glass, of ebonite, or of thin cardboard at S, at right angles to the lens L_2, and is focused on a second or check receiver. The metal screens S_1 and S_2 were necessary only for wave-lengths greater than one centimeter.

Lenses and mirrors were adjusted as follows: After the lenses were cast and turned to fit a given template and before removal from the lathe, a two mm hole was drilled along the axis of rotation of each lens. A frame bearing two properly centered diaphragms, lighted from behind, was fitted to replace the oscillator case on the optical bench. The light pencil directed by these diaphragms defined the optic axes of the system; after passing through the hole in L_1, it was reflected in succession from mirrors at A and B, then passed through L_3 and fell upon the receiver at M. The mirrors A and B and the optical bench carrying the oscillator case and lens L_1 are provided with micrometer adjustments for rotation about vertical and horizontal axes. Lenses L_2 and L_3 are provided with slow motion vertical and horizontal adjustments. The adjustment obtained by using the pencil of light rays has been found to agree with that subsequently obtained by the more tedious method of experimental trial and error. Slightly tilting the common plane of the interferometer mirrors affords a convenient method for obtaining energy equality between the two beams reflected from the Boltzmann interferometer and brought to focus at M.

A Hertzian oscillator, especially a short wave oscillator, because of its rapid wearing away and constant need of readjustment, is very erratic

and unsteady in action. It can in no sense be called either a constant source of radiation or even a uniformly varying source. Consequently the experimental procedure followed by earlier short wave experimenters has led at best to results which were only in the roughest sense quantitative. In the present experiments, a check was kept at all times on the emission of the oscillator by the "check receiver" mentioned above. In any given series of observations, the main and check receivers were made of nearly identical construction. Thus for every excitation of the oscillator, the deflections of both main and check receivers were recorded. The ratio of these two deflections gives a quantity free from any error due to variable emission of the oscillator. Since nearly equal deflections of the main and check receivers offer the best conditions for accuracy, the material of the reflector at S was so chosen as to secure this equality.

In the interpretation of electric wave interference curves, it is important to know something of the relative influence on curve form of the fundamental and upper partials of the oscillator and of the receiver. Fig. 7 shows a series of interference curves obtained by using a single receiver

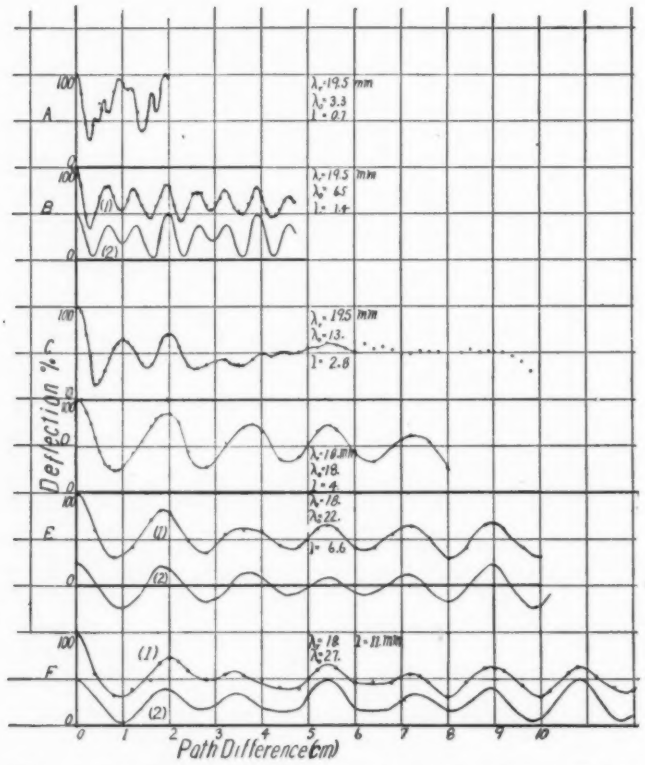

Fig. 7. Interference curves; one receiver and various oscillators.

and a series of different oscillators. The overall length l of the oscillator used and its approximate fundamental wave-length λ_0 are given with each curve. The receiver was of the type shown at *a*, Fig. 3, with vanes made of 1 μ platinum wire 5.5 mm in length, of which about 0.3 mm at each end was embedded in shellac. Its fundamental wave-length λ_r, measured from the different curves, ranges between 18 and 20 mm.

Curve A, Fig. 7.—The curve for this combination of oscillator and receiver exhibits six maxima between zero and a path difference of 19 mm; thus λ_0 equals $\lambda_r/6$, or the fifth upper partial of the receiver. The curve form also shows the presence of the first upper partial and fundamental of the receiver.

Curve B_1, *Fig. 7*, shows three maxima and three minima between the path difference zero and 19.5 mm. Thus as $\lambda_0 = \lambda_r/3$, the oscillator fundamental falls in step with the second upper partial of the receiver. Analysis of this curve, damping neglected, yields the equation

$$Y = \tfrac{1}{3} \cos (2\pi x/\tfrac{1}{2}\lambda_r) + \tfrac{2}{3} \cos (2\pi x/\tfrac{1}{3}\lambda_r),$$

showing that the first upper partial of the receiver is also present with roughly one half the intensity of the second. A plot of this equation appears as B_2, Fig. 7.

Curve C, Fig. 7, shows the fundamental and first upper partial of the receiver. There is no clear indication of any maximum due to the fundamental of the oscillator. The rapid flattening out of the curve is doubtless attributable to the complete disagreement between the fundamental wave-lengths and upper partials of oscillator and receiver.

Curve D, Fig. 7.—The oscillator fundamental, $\lambda_0 = 18$ mm approximately, was near enough to λ_r to give a regular curve of simple form and sustained amplitude, showing the receiver to be in fair resonance with the oscillator.

Curve E_1, *Fig. 7.*—The fundamental of the oscillator with which this curve was made was somewhat longer than that of the receiver but yet near enough to give a curve of well-sustained amplitude though not altogether simple in form. Curve E_2, Fig. 7, is drawn from equation $Y = \frac{2}{3} \cos (2\pi x/\lambda_r) + \frac{1}{3} \cos (2\pi x/\lambda_0)$, where $\lambda_0 = 21.6$ mm and $\lambda_r = 18$ mm, which gives a close enough match with E_1 to show (1) that the wave-lengths assigned in this instance to oscillator and receiver are accurately chosen and (2) that the receiver has roughly twice as much effect upon the form of the curve as the oscillator.

Curve F_1, *Fig. 7.*—Here $\lambda_0 = 3\lambda_r/2$ nearly, and the amplitude is well sustained and yields a curve form of unusual interest. Curve F_2 is drawn from $Y = \frac{2}{3} \cos (2\pi x/\lambda_r) + \frac{1}{3} \cos (2\pi x/\lambda_0)$, where $\lambda_r = 18$ mm

and $\lambda_0 = 27$ mm, which, damping neglected, affords a very close reproduction of F_1.

Irrespective of the different dimensions and characteristics of the oscillators used, all the interference curves in Fig. 7 show a strong maximum at a path difference of about 19 mm or λ_r, indicating plainly that the receiver, because it is less damped than the oscillator, exerts the predominant influence upon the form of the interference curves and upon the fundamental wave-lengths and upper partials thus measured.

Consideration of Fig. 7 and of the foregoing discussion shows that interference curves of simple and regular form and of sustained amplitude are obtained only when the fundamental periods of oscillator and receiver fall close together or when the oscillator fundamental is in close agreement with the first or second upper partial of the receiver. It thus appears that the radiation from the oscillator is highly damped and though not aperiodic may be thought of as a pulse or, even more accurately, as a

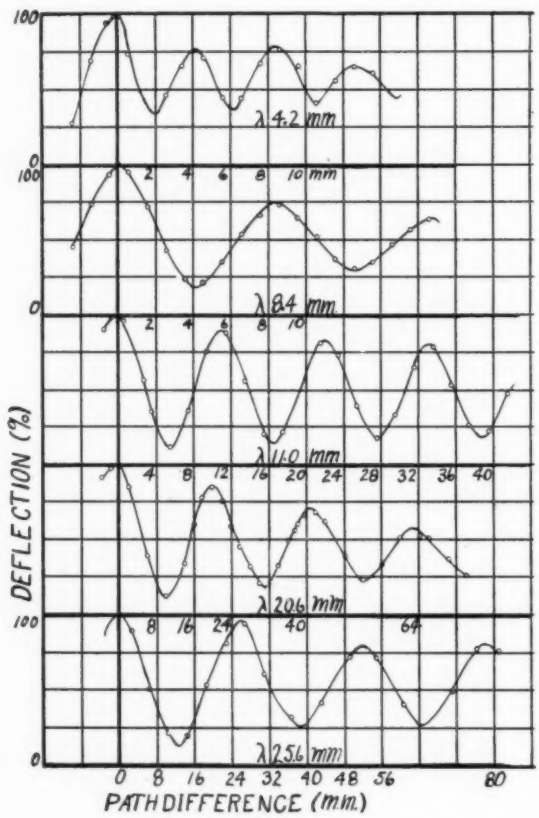

Fig. 8. Set of curves, λ 4.2 to λ 27.

very short wave train with from 60 to 80 per cent of the energy concentrated in the first half wave-length. Upon reflection from the two halves of the interferometer mirror, each pulse is divided into two parts, one following the other by a known time interval. When the time separation of the two pulses is equal to or a small multiple of a natural period of the receiver, we may expect a maximum response. Were the receiver heavily enough damped to be aperiodic, the interference curve would give a measure of the wave-length of the unmodified radiation of the oscillator. Since the receiver is but slightly damped and the oscillator not altogether aperiodic, the interference curve obtained is a compromise of the two effects, in which the receiver is much the larger factor.

These considerations find further illustration in Fig. 8. Curves *A* and *B* were taken with different oscillators but with the same receiver, the fundamental wave-length of which was $\lambda_r = 8.4$ mm. In curve *A*, the fundamental wave-length of the oscillator is 4.2 mm, corresponding to the first upper partial of the receiver. In the remaining curves *C*, *D*, and *E*, the fundamentals of oscillator and receiver were in close agreement.

The observations from which curve *A* is plotted are given in Table I.

TABLE I

Int. mirror setting	Main receiver (*M*)	Check receiver (*C*)	$\frac{M}{C}$	Deflection, per cent
8.5 mm	58 mm	118 mm	.49	60
8.	40	76	.53	65
7.5	36	78	.46	56
7.	26	78	.33	40
6.5	53	93	.58	71
6.	34	56	.61	74
6.	96	147	.65	79
5.5	55	93	.59	72
5.	37	103	.36	44
4.5	32	97	.33	40
4.5*	47	126	.37	45
4.	59	103	.57	70
4.*	44	72	.61	74
3.5*	66	115	.57	70
3.	45	120	.37	45
3.*	41	109	.38	46
2.5	32	123	.26	32
2.5*	29	120	.24	29
2.	76	127	.60	73
1.5	82	100	.82	100
1.	55	99	.56	68
0.5	26	119	.22	27

They show something of the sensitiveness and behavior of the receiver and the general character of the work with short electric waves, and thus afford a basis for judging the results obtained. Column 1 gives the scale readings of the movable upper interferometer mirror plotted as

abscissas in curve *A*; column 2, the corresponding deflections of the main receiver; and column 3, the deflections of the check receiver. Column 4 shows the ratio, and column 5 the so-called deflection percentages plotted as ordinates in the curve. The starred values constitute a second series of interferometer settings.

The arrangement of apparatus used is shown in Fig. 6. The total length of path from oscillator to main receiver, including two reflections, was 180 cm. By means of the time switch, previously referred to, the oscillator was operated for one half second for each deflection. If we take the average of the sum of the deflections of the main and check receivers for maximum points in the interference curve, we get the equivalent of 200 scale divisions on a meter distant scale. The corresponding combined deflection for a 1.5 second exposure was roughly 600 divisions, a remarkably high degree of receiver sensitiveness for waves of this length. The irregular emission of the oscillator is plainly seen in the varying numbers of column 3. Were the oscillator a constant source, these check receiver deflections should have shown no variation. The necessity of using a check receiver for quantitative work is thus evident, and yet, so far as we know, this is the first instance of its use in short electric wave experiments, *i.e.*, with waves less than 4 or 5 cm long.

Upper partials of short wave-length.—Upon continued use, the inner ends of the oscillator doublet at the oil gap become badly pitted and sometimes develop notches or "teeth." This tendency is more marked for platinum than for tungsten electrodes. With increased pitting and "teething" the normal oscillations become less sustained, and the interference curves show the presence of radiation of much shorter wave-length though the curves are seldom of regular pattern. Möbius (4) has thus obtained interference curves which suggest the presence of radiation of a wave-length hardly more than one per cent of the fundamental of his oscillator.

Curve *A*, Fig. 9, was taken with an oscillator of fundamental wave-length about 4 mm operated with a long spark gap between badly pitted platinum electrodes. The receiver elements were thin platinum deposits on mica of type *e*, Fig. 3, and though in action the receiver showed high resistance damping, it had a fundamental wave-length of about 8 mm. The deep minimum and succeeding maximum are evidently due to the receiver. Interferometer settings were made near together for only the first two millimeters displacement. If from the observed deflections the function $60 + 40 \cos (2\pi x/4)$ is subtracted, curve *B*, Fig. 9, is obtained, which plainly indicates the presence of a component of wave-length 0.8 mm. As $\lambda_0/5 = \lambda_r/10 = 0.8$ mm, we apparently have the

fourth upper partial of the oscillator falling in with the ninth upper partial of the receiver.

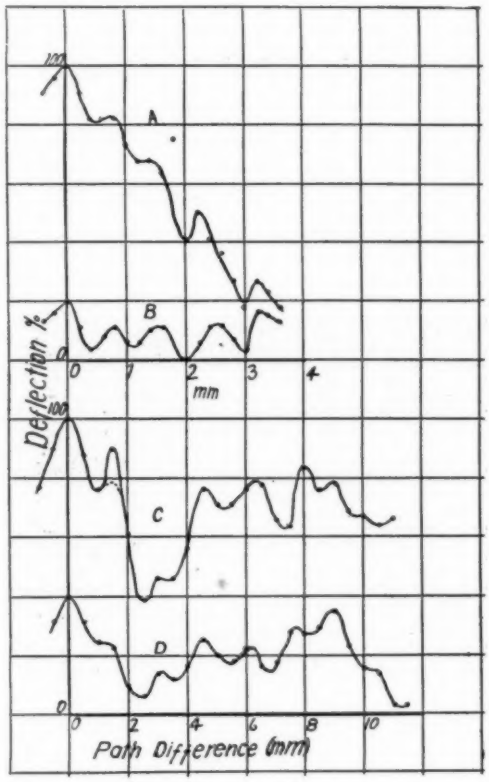

Fig. 9. Harmonics.

For Curve *C*, Fig. 9, the receiver elements, of 1 μ platinum wire, were of type *a*, Fig. 3, and the fundamental wave-length was 7.5 mm. The fundamental of the oscillator was 4.5 mm, the tungsten electrodes were badly worn, and the spark gap long. Emission had fallen to 20 per cent of its initial intensity. Curve *D*, Fig. 9, is the sum of three harmonic curves corresponding to the equation

$$Y = 2/5 \cos (4\pi x/7.5) + 2/5 \cos (4\pi x/4.5) + 1/5 \cos (4\pi x/1.5).$$

Its resemblance to Curve *C* is sufficiently close to show three components 7.5, 4.5, and 1.5 mm; the first is the fundamental of the receiver, the second that of the oscillator, and the third is formed by the second upper partial of the oscillator falling in with the fourth upper partial of the receiver.

A reflecting echelon.—The degree of damping which determines the form of the pulse or short wave train for electric waves in air has been studied by Hull,[10] Bartenstein,[11] and Ives.[12] The results obtained by these investigators agree as to the general nature of the radiation; but because of the different forms of oscillators used by them, and because the influence of the receiver upon the interference curve was not in all cases satisfactorily eliminated, their results show a wide variation in the degree of damping reported. As a further means for analyzing the wave form and content of the emission of very short wave oscillators, a reflecting echelon grating was constructed of eight carefully machined and polished brass blocks bearing against a strip of plate glass as shown in Fig. 10. The inclination of this glass plate and with it the equivalent

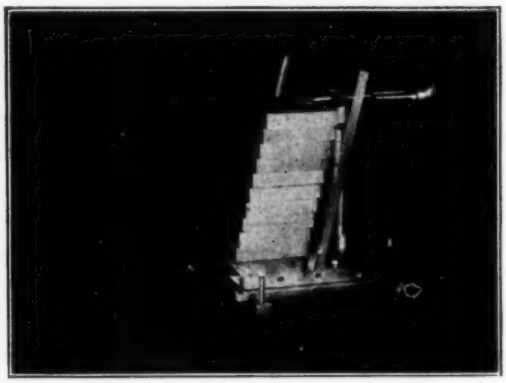

Fig. 10. Photo of echelon.

grating space or tread of the steps could be varied by means of a micrometer screw shown in the figure. In use this echelon is placed in the optical path at *B*, Fig. 6. If the tread of the steps is made equal to half the fundamental wave-length of the incident radiation, the original pulse or short wave train is divided into eight trains one following another at intervals of one oscillator cycle. For purposes of illustration, the damping is assumed to be such that the amplitude falls to 1 per cent of its initial value in four cycles. The calculated resultant wave form obtained by adding the displaced 8 wave trains is shown in Fig. 11. The echelon thus serves to isolate the fundamental wave emitted by the oscillator and to render it more nearly monochromatic. If a receiver with a very much longer fundamental than that of the oscillator is used,

[10] G. F. Hull, Phys. Rev. **5**, 231–46, 1897.
[11] Bartenstein, Ann. der Phys. **29**, 201, 1909.
[12] Ives, Phys. Rev. **31**, 185, 1910.

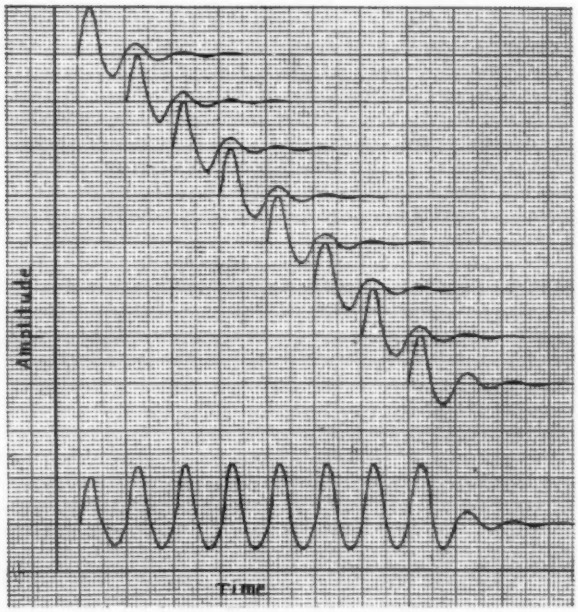

Fig. 11. Addition of pulses.

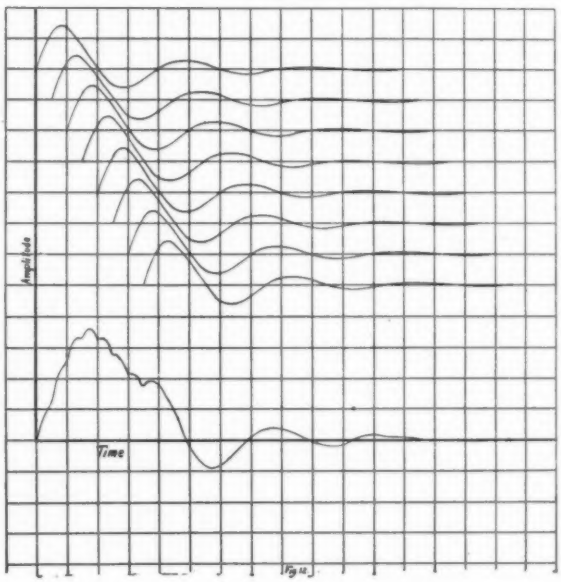

Fig. 12. Addition of pulses λ/16.

and the tread of the echelon is set for a path difference equal to the fundamental of the receiver, the result obtained will correspond to the characteristics of the receiver, irrespective of the characteristics of the oscillator. In this way it is possible to get a clear regular interference curve corresponding to the fundamental of the receiver even when no radiation anywhere near it in wave-length exists in the emission of the oscillator. The wave-length thus obtained is therefore wholly spurious in that it is manufactured by the echelon and receiver and is not emitted by the oscillator. While it is thus possible to get almost any wave-length to which the receiver responds, which is longer than that emitted by the oscillator, it is not practicable by use of the echelon to get waves very much shorter than the fundamental emission of the oscillator and its accented upper partials. Fig. 12 shows the computed resultant wave train due to setting the echelon tread at 1/16 of the fundamental wave-length of the oscillator. In it the fundamental of the oscillator appears as a ground wave and, superimposed upon it, are ripples 1/8 as long as the fundamental.

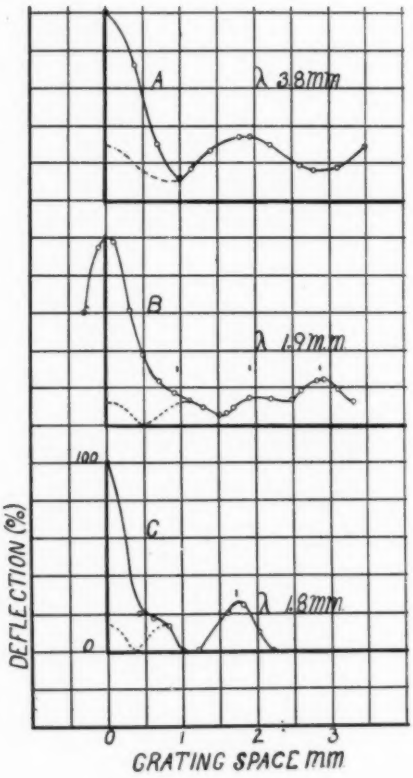

Fig. 13. Step curves.

The echelon method has been used to measure the fundamental wave-lengths and to analyze the radiation of a number of oscillators. In these experiments the receiver employed is of type *C*, Fig. 3, consisting of five parallel strands of 1 μ platinum wire. The various oscillator doublets employed consisted of tungsten cylinders, the smallest of which was 0.2 mm in diameter and 0.2 mm long. These were embedded in the glass tube ends for only about one half their length. The measured wave-lengths of curves *A*, *B*, and *C*, Fig. 13, were 3.8, 1.9, and 1.8 mm, respectively. Curve *B* was carried out to the third order. That a third maximum appears indicates that the radiation is less damped than that previously assumed and shown in Fig. 11.

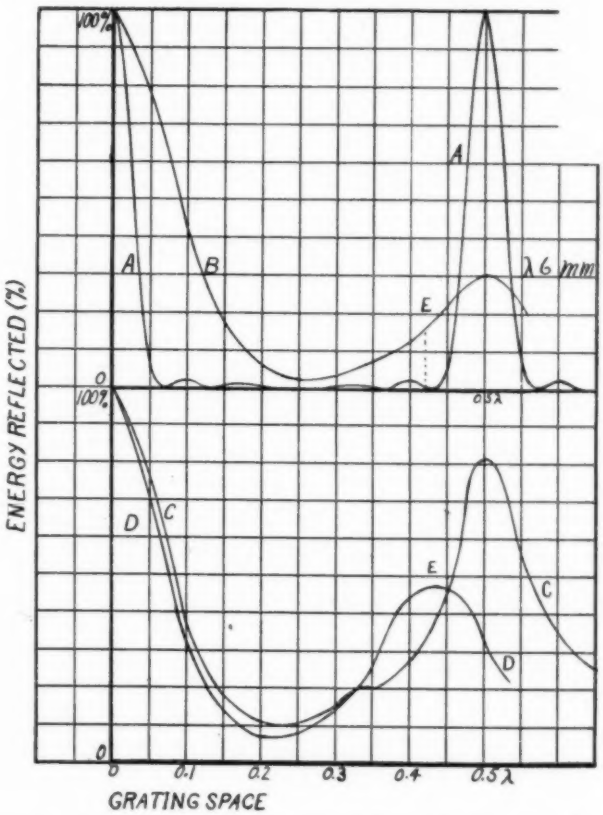

Fig. 14. Analysis of radiation (1) with echelon; (2) with crossed echelons.

To get higher resolving power for further analysis of the oscillator emission, a second echelon was constructed and the two used in series, the first placed at *A*, Fig. 6, with steps vertical, and the second at *B*, with steps horizontal. The width of tread of the first was set equal to

half the fundamental wave-length of the oscillator λ_0, obtained from the position of the maximum in curve *B*, Fig. 14. The tread width of the second echelon was then varied continuously and curve *C*, Fig. 14, taken. The first maximum of curve *C* rises to within 80 per cent of the value of the first maximum of curve *A* computed for monochromatic radiation, thus showing an unexpected degree of homogeneity. The tread of the steps of the first echelon was then set for a width equal to $0.85\lambda_0/2$, requiring a maximum of the first order to fall at *E*. The tread width of the second echelon was then varied and curve *D*, Fig. 14, taken. The first maximum falls at the required place and rises to about 45 per cent of the theoretical maximum in curve *A*. This shows the influence of the first echelon upon the incident radiation, although after leaving the echelon, the radiation is less homogeneous in this case than in Fig. 14*c*. The procedure illustrated in Figs. 14*c* and 14*d* shows that the crossed echelons may be used to obtain radiation of wave-length somewhat less than the fundamental of the oscillator employed. The echelon principle also promises substantial assistance in the further difficult progress towards shorter waves, by making possible the singling out of higher upper partials from the complex emission of the oscillator. It is easier to build radiometric receivers tuned for very short waves than to construct oscillators to correspond. Hence the echelon together with very short tuned receivers offers the best arrangement so far realized for bringing the electric wave spectrum and the heat spectrum together.

The difficulty of building oscillators for very short electric waves lies not only in being able to handle and seal into glass such minute metal cylinders, but even more in the fact that the ratio of the fundamental wave-length of an oscillator to its total length is a ratio which for waves less than one centimeter increases rapidly as we go to higher and higher

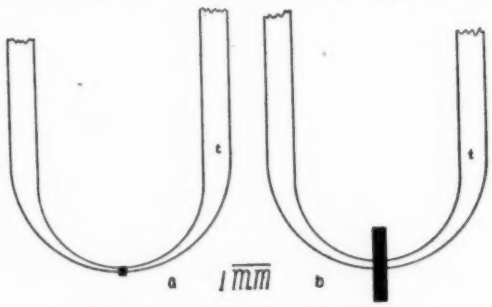

Fig. 15. Sketch of oscillator seal.

frequencies. Thus Figs. 15*a* and 15*b* show halves of two typical oscillator doublets *c*, of which 15*a* is for very short and 15*b* for longer waves. When mounted in the oscillator box, that portion of the doublet of oscillator 15*b*, for instance, which projects from the glass tube *t*, into which

it is sealed, is emersed in oil, another part of the length is embedded in glass, and the remainder, which extends into the interior of the tube, is surrounded by air. This gives a complex capacity involving three different dielectric media. In an oscillator of the proportions of 15*b*, the fundamental wave-length divided by the overall length of the doublet λ_0/l has in our experiments run as low as 2.7 for wave $\lambda_0 = 27$ mm, while in such a case as Fig. 15*a*, $\lambda_0 = 2$ mm, a larger proportion of the doublet cylinders are of necessity embedded in glass, hence the capacity is proportionately larger and λ_0/l has in some instances run as high as 4.8. As we go to smaller and smaller oscillators, therefore, this rising ratio makes progress toward shorter and shorter waves increasingly difficult.

Table II. exhibits data concerning oscillator dimensions and measured

TABLE II

Oscillators referred to as "*M*" are oscillators described and used by Möbius. "*La*" refers to Lampa oscillators, and "*Le*" to Lebedew's oscillators; the remainder are oscillators described in the present paper.

Observer or oscillator	λ_0 measured	l, length of oscillator	Diameter	Length of glass seal	λ_0/l
Fig. 8*E*	27 mm	10 mm	0.5 mm	1 mm	2.7
Fig. 8*D*	21.6	6.6	0.5	0.8	3.3
M	16.2	4.5	0.5	2	3.6
La	8	4	0.5	2	2
Fig. 8*C*	11	4	0.5	0.6	2.8
La	6.1	3	0.5	1.5	2
Fig. 8*B*	8.4	2.8	0.5	0.6	3
Le	6	2.6	0.5	—	2.3
La	4	2	0.5	1	2
M	7	1.98	0.5	1	3.5
Fig. 8*A*	4.2	0.85	0.25	0.4	4.9
Fig. 13*B*	1.9	0.4	0.25	0.2	4.8
Fig. 13*C*	1.8	0.4	0.25	0.2	4.5

wave-lengths. Column 1 contains the designation of the different oscillators listed, including several oscillators used by other investigators; column 2 gives the corresponding measured wave-lengths reported; column 3, the overall length of the oscillator; column 4, the diameter of the oscillator cylinders; column 5, an estimate of the length of the glass seals; and the last column gives the ratio of column 2 to column 3. If probable values be assigned to the λ_0/l ratio for the Lebedew [2] and Lampa [3] oscillators, it seems very probable that both investigators underestimated the wave-lengths with which they were dealing. Möbius' [4] shortest oscillator of platinum cylinders 1.98 mm long and 0.5 mm in diameter, giving a measured fundamental wave-length of 7 mm, seems to be the smallest oscillator previously used. A ten-year-old rumor

concerning 2 mm fundamental waves obtained by Von Baeyer [13] apparently still lacks confirmation.

The chart shown in Fig. 16 displays the present stage of progress

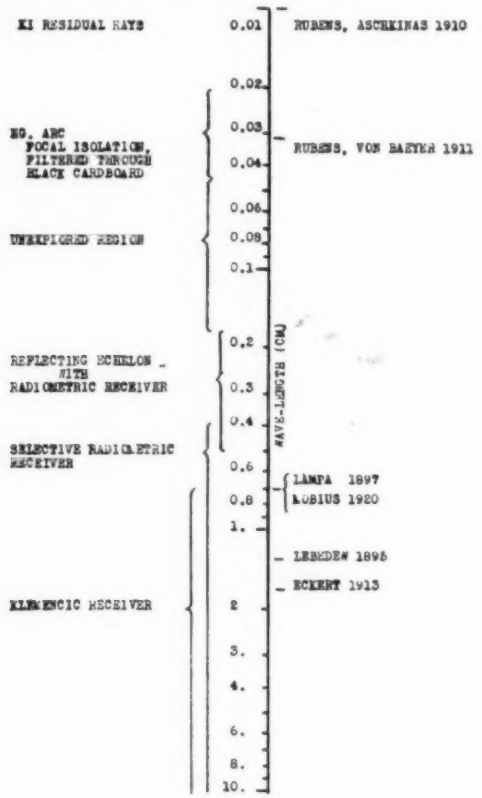

Fig. 16. Spectrum chart.

toward closing the gap still separating the infra-red from the electric wave spectrum. Neglecting wave-length measurements on upper partials which are ripples on a longer fundamental wave, the present experiments have reduced the measured fundamental wave-lengths from 7 mm, reached by Lampa and Möbius, to 1.8 mm, an interval of two octaves. Progress over an interval of two more octaves will connect the electric wave spectrum to Rubens and Von Baeyer's longest heat waves.

The writers are indebted to Miss Ruth Sublett and Miss Marion Smith, assistants in the laboratory, for help in taking observations at the check receiver.

NELA RESEARCH LABORATORIES,
NATIONAL LAMP WORKS,
CLEVELAND, OHIO
December 13, 1922

[13] H. Rubens, Physik: Kultur der Gegenwart, p. 203, Leipzig, 1915.

THE OPTICAL CONSTANTS OF CERTAIN LIQUIDS FOR SHORT ELECTRIC WAVES

By J. D. Tear

Abstract

Optical constants of liquids for short electric waves of length 4 to 27 mm were measured by use of special Hertzian oscillators and radiometer receivers developed by Nichols and Tear, *for water, glycerin, and methyl and ethyl alcohol.* For the extinction coefficient, glass and ebonite cells were used; for the coefficient of reflection, the liquid was held in a tilted rubber tray. The refraction indices were then computed by the Cauchy-Quincke formula. In a few cases the index was determined directly from measurements of the reflection from a thin layer of the liquid over a mercury surface as a function of the thickness, since, due to interference, maxima occur at intervals of half a wave-length, providing the absorption is not too great or the reflection too small. Water shows absorption maxima at wave-lengths of 20, 7 and perhaps 2 mm; its index drops from 8.7 for 40 mm to 5.3 for 4 mm. The experimental values agree with those computed by Rubens from the Debye theory for $\lambda > 40$ and $\lambda < 0.2$ mm; the discrepancies in the intermediate region are evidently due to the presence of two or three absorption bands, whereas only one was assumed.

THE great change in refractive index of a number of liquids in crossing the unexplored region separating the extreme infra-red from the shortest electric waves is of considerable interest and has claimed the attention of many investigators. A notable example is the dispersion of water, the index of refraction changing from a value near 1.5 in the infra-red to approximately 9 for wave-lengths of a few centimeters. The study of the optical constants of these liquids has extended from wave-lengths of several meters to about two centimeters, but in much of the earlier work the method of waves on parallel wires was used.[1]

Lebedew [2] and Lampa [3] in their measurements of indices of refraction used prismatic cells of small angle. Later experimenters, following the lead of Cole,[4] used the method of reflection, only Eckert [1] and Möbius [5] taking into consideration the absorption coefficients. The unfortunately wide variation in the results of the various investigators may be accounted for in part by the errors introduced by diffraction when the reflecting

[1] Eckert, Verh. d. Deut. Ges. **15**, 307 (1913), gives complete bibliography.
[2] Lebedew, Wied. Ann., p. 1 (1895).
[3] Lampa, Wiener Ber. **105**, pp. 587 and 1049 (1896).
[4] Cole, Wied. Ann. **57**, p. 290 (1896).
[5] Möbius, Ann. d. Phys. **62**, p. 293 (1920).

and refracting surfaces used are but a few wave-lengths in extent and in part by the inherent difficulties in using a small Hertzian oscillator the emission of which tends to vary both in amount and in the degree of damping.

The principal source of error lies in the determination of the wave-length of the radiation used. Some of the early wave-lengths appear to be in error by a factor as large as two. Because of the influence of the receiver characteristics upon the interference curves obtained, such curves have been often misinterpreted. To eliminate the effect of the receiver upon the wave-lengths measured it is necessary either to use a receiver which is perfectly non-selective, a condition difficult to realize, or to use an oscillator and a selective receiver which are carefully tuned to the same frequency. Eckert has used the latter method and has obtained apparently reliable data for wave-lengths ranging from 80 to 17 mm.

Rubens[6] in 1915, collecting the electric wave data published at that time and using his own data for the extreme infra-red, endeavored to put to an experimental test Debye's theory of the dispersion of liquids.[7] According to the theory of Debye the molecules of a liquid are electrical dipoles, the directions of their axes being maintained in a chance distribution by thermal agitation, and consequently upon the application of an electric field, the molecules come to their new position of equilibrium only after a finite time. This leads to a value of the index of refraction which is a function of wave-length and temperature. Rubens' computed and experimental values for the index of refraction of water agreed well. However, the data then available did not extend into the region in which the large change in refractive index occurs.

Recent developments in electric wave technique have made it possible to follow the course of dispersion curves several octaves toward shorter wave-lengths. In general two methods have been employed. In the first the index of refraction has been computed from measured values of the absorption and reflection coefficients, and in the second the phenomenon of interference in thin films has been utilized.

Apparatus.—The source consisted of an improved form of the Hertzian oscillator which was used in conjunction with a recently developed receiver of the radiometer type. Descriptions of the source and of the receiver, and also the procedure followed in obtaining interference curves for the wave-length measurements are given in detail in the preceding paper.[8] The method of securing homogeneous radiation has been to

[6] Rubens, Ber. d. Deut. Phys. Ges. **17**, p. 315 (1915).
[7] Debye, Verh. d. Deut. Phys. Ges. **15**, 777 (1913).
[8] Nichols and Tear, Phys. Rev., **21**, p. 587 (1923).

use a selective receiver to which the oscillator was carefully tuned. The interference curves for five of the six wave-lengths used in the present experiments are shown in Fig. 1. The form of the curves affords

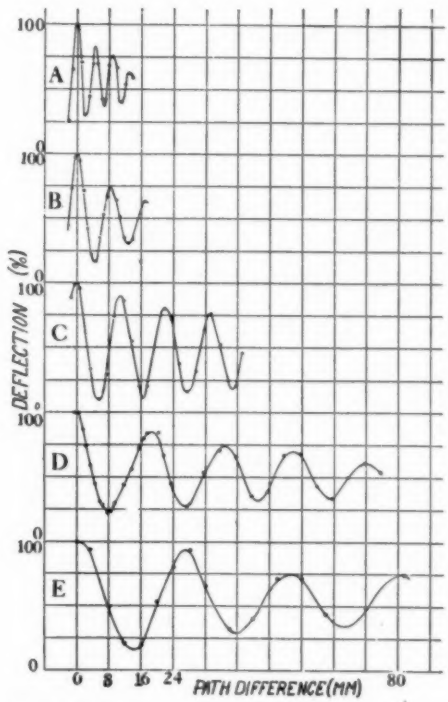

Fig. 1. Boltzmann interference curves. A, $\lambda = 0.42$ cm; B, $\lambda = 0.84$ cm; C, $\lambda = 1.1$ cm; D, $\lambda = 1.8$ cm; E, $\lambda = 2.7$ cm.

a basis for estimating the purity of the radiation and the accuracy of the wave-length measurements.

Transmission Measurements.—The arrangement of apparatus for the transmission measurements is shown in Fig. 2. The radiation from the

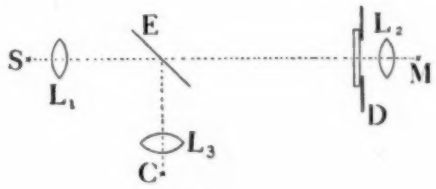

Fig. 2

source at S is converged into a parallel beam by the paraffin lens L_1. A definite fraction is reflected by the screen of ebonite or glass at E toward the check receiver C which is at the principal focus of a paraffin lens L_3;

the beam traversing E falls upon the cell and is brought to a focus by lens L_2 upon the main receiver at M. Immediately behind the cell is a diaphragm D to limit the portion of the beam used and to protect the receiver from stray radiation.

The procedure was, briefly, as follows. The source was operated for chosen intervals of time ranging from one fifth to one second, and the deflections of both main and check receivers were noted. The ratio of these deflections (M/C) was taken first with the cell removed and then with the cell in place. The quotient of these two ratios was taken as the transmission of the cell. The strict proportionality between deflections and incident energy for this type of receiver has previously been carefully tested and found to hold within one per cent.

Two types of cells were used. The first series was made up with walls of plate glass six millimeters thick. Some of the transmission measurements thus obtained are given in Fig. 3. As the ordinates are

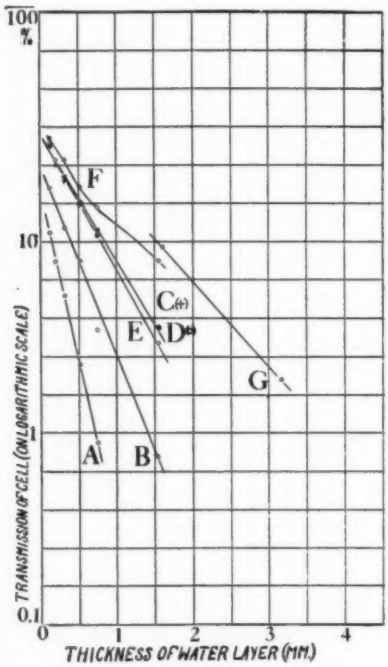

Fig. 3. Transmission of water for electric waves. A, $\lambda = 0.42$ cm glass absorption cell; B, $\lambda = 0.84$ cm glass absorption cell; C, $\lambda = 1.1$ cm glass absorption cell; D, $\lambda = 1.5$ cm glass absorption cell; E, $\lambda = 1.8$ cm glass absorption cell; F, $\lambda = 2.7$ cm glass absorption cell; G, $\lambda = 2.7$ cm ebonite absorption cell.

plotted on a logarithmic scale, the slope of the line gives a measure of k in $I = I_0 e^{-kd}$, in which I_0 is the energy which enters and I is that which

has traversed a layer of the liquid of thickness d. As we are interested only in the slope of the line, it has not been necessary to correct the measurements for the loss by reflection at the cell walls or on entering the liquid.

The reflection from both glass and water surfaces is high and so it is only because of the low transmission of the liquid that the transmitted energy does not pass through interference maxima and minima as the cell thickness is varied. For ethyl alcohol and glycerin which have lower coefficients of absorption and for water for wave-lengths greater than 25 mm (F, Fig. 3), the interference effects are noticeable. In order to check the results obtained with the glass absorption cells, a second series of cells was made up with ebonite walls. As the refractive index of ebonite (1.6) is low compared to that of glass (2.4), the interference effects due to reflection were smaller for the ebonite than for the

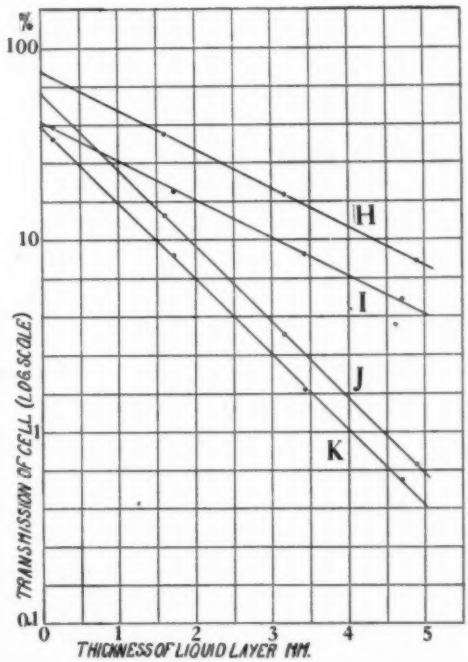

Fig. 4. Comparison of transmissions as measured with glass and with ebonite absorption cells. $\lambda = 0.84$ cm. H, ethyl alcohol ebonite cells; I, ethyl alcohol glass cells; J, methyl alcohol ebonite cells; K, methyl alcohol glass cells.

glass cells. Because of their lower reflecting power the transmission of the ebonite cells for a given thickness of liquid layer was of course greater than that of the glass cells. In Fig. 4 is shown the results of the measurements made with the two types of cells. The slopes of the two sets of

lines agree satisfactorily. The differences in the values of k computed from the lines as drawn are somewhat less than two per cent, showing the values of the absorption so measured to be free from any considerable error due to reflection from the cell walls.

Reflection.—The reflection measurements were made by comparing the reflection from the surface of the given liquid to that from a mercury surface. Eckert [1] has shown the reflection of mercury for wave-lengths from 17 to 80 mm to be unity to within one half of one per cent. These results together with the high reflection observed for metals for long infra-red waves make it safe to assume 100 per cent reflection for mercury throughout the spectral region of the present measurements.

The oscillator is placed at S, Fig. 5, at the principal focus of the paraffin

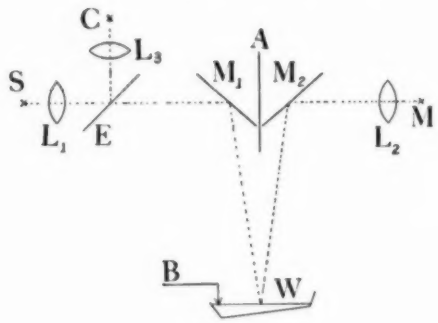

Fig. 5

lens L_1. The disposition of ebonite screen E, paraffine lenses, and the receivers is as shown. M_1 and M_2 are plate glass mirrors with their silvered sides toward the beam; and W is the liquid surface. A sheet metal screen is placed at A to minimize the scattered energy reaching the main receiver. The liquid is contained in a hard rubber tray (15 × 20 cm) which is inclined as shown so that any energy reflected from the lower surface will be directed to one side. There is an indicator at B by which to gauge the height of the liquid in the tray.

To test the effectiveness of the tilted tray in avoiding reflection from the lower liquid surface, reflection measurements were made both with and without a piece of plane sheet metal lying on the floor of the tray. No change in the reflected energy due to the presence of the metal mirror could be observed. The amount of scattered energy which reached the receiver when the tray was empty ranged from 0.8 per cent for 4.2 mm to 0.4 per cent for λ 18 mm. With the tray removed and a 20 × 20 cm piece of sheet metal inclined at an angle of 45° to the horizontal substituted, the receivers gave no deflections. Good evidence that the

amount of scattered radiation reaching the receiver was small when the tray was filled with an absorbing liquid may be obtained from a consideration of the measurements for kerosene, which has a low reflecting power and no measurable absorption. The coefficients of reflection of kerosene observed for three wave-lengths 4, 8, and 18 mm were 0.040, 0.039, and 0.039. Taking the value 2.13 for the dielectric constant and $\sqrt{K}$ or 1.46 for the index of refraction, the coefficient of reflection computed by the Fresnel formula is 0.0353. We are safe, then, in assuming that when an absorbing liquid was in the tray the amount of scattered energy reaching the receiver was less than one half of one per cent.

For each reflection measurement a series of eight ballistic deflections was taken first for mercury and then for the liquid under investigation. A typical series is given below.

TABLE I

Mercury			Water		
Main (M)	*Check (C)*	*M/C*	*Main (M)*	*Check (C)*	*M/C*
194	138	1.41	166	234	.710
156	112	1.39	200	273	.734
188	133	1.41	226	309	.732
183	127	1.44	195	274	.712
190	137	1.39	207	291	.712
223	156	1.43	160	225	.712
253	183	1.38	220	302	.730
224	160	1.40	205	285	.720
Average....		1.41 ± .016			.720 ± .009

Coefficient of reflection 0.510 ± .01.

Index of Refraction.—The Cauchy-Quincke formula [9] was used for computing the index of refraction from the measured values of the absorption and reflection coefficients. For the electric vector in the plane of incidence the formula may be reduced to

$$n = \frac{b}{\cos \phi} + \sqrt{\frac{(b^2 - 1)}{\cos^2 \phi} - (nx)^2},$$

where

ϕ = the angle of incidence;
nx = the extinction coefficient in $I = I_0 e^{-4\pi nx/\lambda d}$;
λ = the wave-length in air;
$b = (1 + R)/(1 - R)$;
R = the coefficient of reflection.

[9] Winkelmann's Handbuch, p. 1300.

This is an approximate formula which holds if n^2 is very much greater than $\sin^2 \phi$, which was the case in all the present measurements, for $\sin^2 \phi$ never exceeded 0.03 and n^2 ranged from 4 to 70. The collected values of R, nx, and n (called n_1) are given in Table II.

TABLE II

	λ in cm	R	nx	n_1	n_2
Ethyl Alcohol.....	0.42	0.087	0.156	1.84	
	0.84	0.125	0.285	2.06	1.95
	1.1	(0.133)	0.277	2.2	
	1.5	(0.145)	0.337	2.15	
	1.8	0.150	0.512	2.2	
	2.7	0.162	0.453	2.27	
Methyl Alcohol....	0.42	0.171	0.39	2.10	
	0.84	0.19	0.55	2.43	2.33
	1.5	(0.215)	0.797	2.52	
	1.8	0.228	1.09	2.7	3.2
	2.7	0.316	0.95	3.3	
Glycerin.....	0.42	0.108	0.147	1.98	
	0.84	0.136	0.252	2.16	2.15
	1.1	(0.145)	0.184	2.2	
	1.5	(1.55)	0.28	2.3	
	1.8	0.154	0.40	2.53	
	1.8	(0.16)	(0.25)	2.23	
	2.7	0.187	0.208	2.53	
Water.....	0.42	0.484	1.28	5.33	
	0.84	0.516	1.49	5.68	
	1.1	0.54	1.44	6.27	
	1.5	0.565	1.83	6.62	
	1.8	0.58	2.32	6.65	
	2.7	0.64	2.26	8.45	

R, coefficient of reflection for angle of incidence of 8° 20′, with electric vector in plane of incidence.
n_1, index of refraction computed from extinction coefficient and R.
n_2, index of refraction as measured by reflection from thin layers.
Values in parentheses were obtained by interpolation.

Reflection from Transparent Liquid Layers over Mercury.—An interesting study which gives a direct though approximate measure of the refractive index and the coefficient of reflection of a liquid and also an estimate of its absorbing power, has been that of the reflection from a mercury surface upon which was floated a liquid layer a few wave-lengths in thickness. The bottom of a cylindrical tray 19 cm in diameter was covered with mercury and the reflection from the mercury surface measured. Known quantities of the liquid to be studied were then added and the combined reflection from the two surfaces observed.

Because of the meniscus of the mercury and that of the second liquid the layer thickness as computed from the quantity of liquid added is

subject to a constant error, making it necessary to extrapolate for zero film thickness. As the first maximum (Fig. 6) corresponding to zero thickness of layer is very sharp, this extrapolation can be done with satisfactory accuracy. The meniscus correction is of the order of 20 cc or in terms of film thickness 0.1 mm.

Curve *A*, Fig. 6, shows the results for ethyl alcohol for λ 8.4 mm.

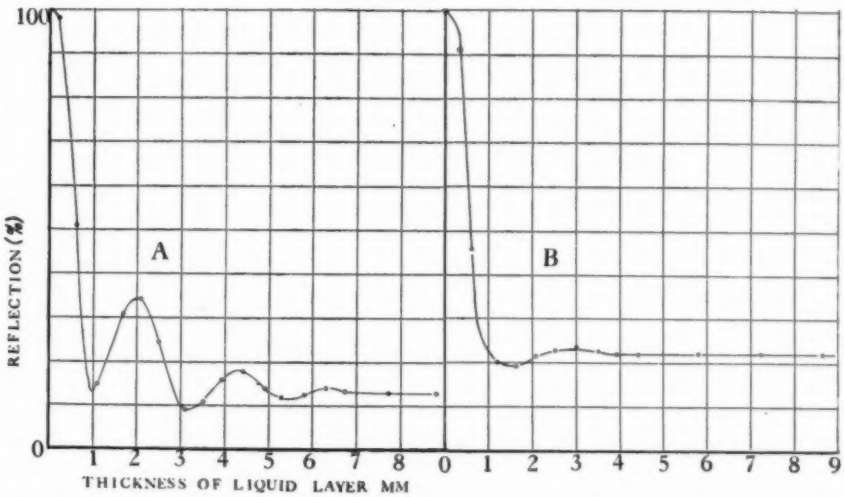

Fig. 6. Reflection from liquid layers over mercury. *A*, ethyl alcohol λ = 0.84 cm; *B*, methyl alcohol λ = 1.8 cm.

In computing the optical path in the liquid we may consider the case as one of normal incidence, for, using 2 as an approximate value of the refractive index, the angle of refraction corresponding to the angle of incidence 8° 20′ is 4° 10′. The average distance between maxima and between minima is 2.14 mm which gives for the wave-length in the liquid $2 \times 2.14 = 4.28$ mm. This divided into 8.4 mm gives 1.96 as the refractive index of alcohol for this wave-length. This value and that computed from the reflection and absorption measurements, 2.06, agree within the limits of error of the method.

Because of the absorption of the liquid, the amplitudes of the successive maxima and minima decrease exponentially and consequently the maxima and minima are displaced from their true position. Because the present measurements with this method are only approximate, it has not been considered necessary to correct for this displacement.

When the liquid layer is sufficiently thick, the transmitted energy is completely absorbed. The curve of the reflected energy then becomes parallel to the horizontal axis at a level corresponding to the reflection coefficient of the liquid under investigation.

Values of the index of refraction of methyl alcohol and glycerin obtained by this method are included in Table II, column headed n_2. The method of reflection from films over a mercury surface is applicable only to those liquids which are sufficiently transparent for layers several wave-lengths in thickness to be used and which have a sufficiently large reflecting power. It proved to be unsatisfactory for kerosene, which, though it shows very little absorption, has a reflecting power of only 4 per cent, and for water, a layer of which one wave-length in thickness is practically opaque for wave-lengths of a few millimeters. Curve *B*, Fig. 6 (methyl alcohol for $\lambda = 18$ mm), shows an instance in which the method is limited by the absorption of the liquid.

Results.—The numerical results are collected in Table II and represented graphically in Figs. 7 and 8. Glycerin, ethyl alcohol, and methyl

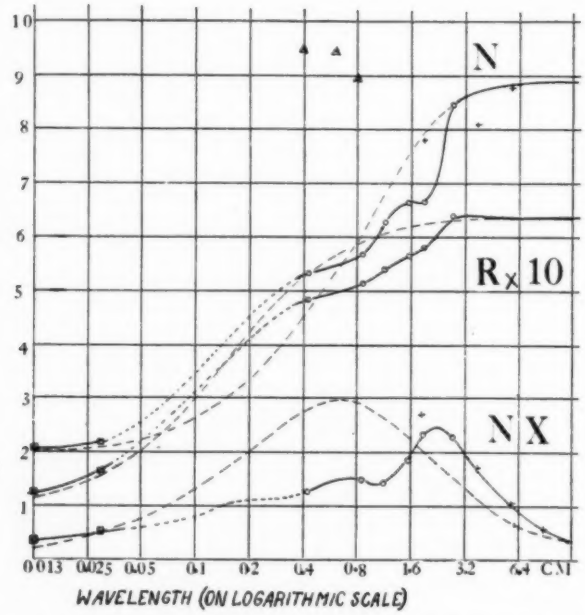

Fig. 7. Index of refraction n, coefficient of reflection R, and extinction coefficient nx for water. The light dashed lines represent values computed by Rubens. □ data from Rubens, + data from Eckert, △ Lampa's values of n.

alcohol in Fig. 8, all show anomalous dispersion in the region studied. Their dispersion curves, however, slope gradually, the index of refraction in each case reaching a value at $\lambda = 0.42$ cm not far from that observed in the visible region of the spectrum. For each of the three liquids there exists a strong absorption band at a wave-length from 5 to 10 cm. Within the range of the present measurements, however, their absorption curves are without large elevations or depressions.

The distinct though low maxima corresponding so closely with those observed for water, as shown in Fig. 7, suggest the presence of water as an impurity. An approximate calculation gives 2 per cent as an esti-

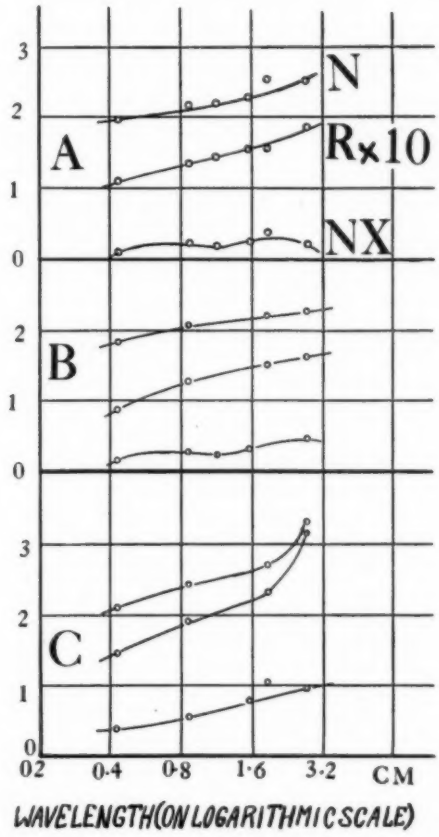

Fig. 8. Refractive index, coefficient of reflection and extinction coefficient for *A*, Glycerin; *B*, Ethyl alcohol; *C*, Methyl alcohol.

mate of the amount of water necessary to produce the observed absorption maxima for ethyl alcohol and glycerin. The corresponding figure for methyl alcohol is 10 per cent. Although the alcohols used were specified by the manufacturer as "absolute," it is possible that the amount of water absorbed from the atmosphere in the process of filling the cells, together with that initially present, may have reached 2 per cent. However, in the case of methyl alcohol it is improbable that the percentage of water necessary to produce the observed values of absorption which lie above the general level of the curve was present, and the low absorption maximum observed near λ 2 cm is doubtless real.

The transmission data for water (Fig. 7) place a strong absorption band at λ 2 cm and a weaker one near λ 0.7 cm though there are not enough observed points in this region to determine the position of the second band closely. The portion of the curve drawn from electric wave data is connected by a dotted line with the values obtained by Rubens in the infra-red.[6]

The indicated points on the dispersion curve n, Fig. 7, are computed from measured values of the reflecting power R and the extinction coefficient nx. To determine the course of the curve more definitely, additional points were computed from interpolated values of R and nx. The index of refraction decreases from its high value 9 for very long waves to the value 5.3 for λ 0.42 cm by a series of steps, each step corresponding to an absorption band. From the course of the dispersion curve at λ 0.4 cm and at λ 0.01 to 0.03 cm as determined by Rubens, a third step corresponding to an absorption band near λ 0.2 cm is indicated.

The values of n obtained by Eckert [1] and Lampa [3] are included in the chart. The location of Lampa's observed points seems to show Lampa's shortest waves even longer than the 7 mm assigned to them by Möbius.

It is of interest to compare, in Fig. 7, the observed n, R, and nx curves for water with those computed by Rubens from Debye's theory.[6] The observed and computed curves agree well in the extreme infra-red and for wave-lengths greater than 4 cm, regions well removed from the principal absorption band. The discrepancies in the intermediate region are evidently due to the assumption, for purposes of computation, of a single absorption band rather than the threefold one suggested by the present measurements.

The writer wishes to express his gratitude to Dr. E. F. Nichols for his constant interest and many helpful suggestions, and to Miss Ruth Sublett and Miss Marion Smith for their assistance in taking the observations.

NELA RESEARCH LABORATORIES,
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CLEVELAND, OHIO,
December 20, 1922

ELECTRON EMISSION FROM METALS AS A FUNCTION OF TEMPERATURE

By Saul Dushman

Abstract

Electron emission from metals as a function of temperature.—(1) *General equation.* The emission of electrons from a metal may be considered as thermodynamically equivalent to the evaporation of a monatomic gas, for which an equation is derived on the basis of the Nernst heat theorem. If it is assumed that the specific heat of free electrons in the metal is negligible while the specific heat of the evaporated electrons is the same as that of a monatomic gas, the equation assumes the simple form $I = AT^2\epsilon^{-b_0/T}$, where $b_0 = \varphi_0 e/k$ (e is electronic charge, k is the Boltzmann constant, and $\varphi_0 = \varphi - \frac{5}{2}kT/e$, where φ is the Richardson work function). An equation of this form has been suggested before but not on the same theoretical grounds and a different value of A has been obtained. Its chief advantage over the usual Richardson equation, $I = A_1T^{1/2}\epsilon^{-b/T}$, where $b = \varphi e/k$, is that A is theoretically a universal constant. (2) *The value of the universal emission constant A* is computed in two ways. Using the Sackur-Tetrode equation for the chemical constant i_0, A comes out 60.2 amp./cm² deg.², while the theory of rational units of Lewis, Gibson and Latimer gives 50.2 amp./cm² deg.². Recent experimental results of Davisson and Germer, and of Schlichter as well as data obtained by the writer agree with the new equation as well or better than with the old, but the temperature scale is not sufficiently accurately known to distinguish experimentally between the two values of A. (3) *The relation between A and the chemical constant* i_0 (or C_0) is derived.

Values of the work function in equivalent volts have been computed from the experimentally determined values of b_0, for *tungsten* (4.53), *thorium* (2.94), *molybdenum* (4.31), *tantalum* (4.40), and *calcium* (2.24) within ½ to 1 per cent. The values for *uranium* (3.28), *zirconium* (3.28), *yttrium* (3.19) and *cerium* (3.07) are upper limits. In general, the values are lower the larger the atomic volumes. Experimental details will be given later.

Part I. Derivation of General Equation

Application of Nernst heat theorem to monatomic vapors.—On the basis of the second law of thermo-dynamics it has been shown that the heat of vaporization may be calculated by means of the well-known relation

$$L = RT^2\frac{d \log P}{dT}, \qquad (1)$$

where L = heat of vaporization per gram-molecular weight at the absolute temperature T;

R = gas constant per gram-molecular weight = 1.987 cal./deg.;

p = vapor pressure at temperature T.

If C_p denotes the specific heat of the vapor at constant pressure, and c_p that of the solid (or liquid), L can be expressed as a function of T by the following relation:

$$L = L_0 + \int_0^T C_p dT - \int_0^T c_p dT. \tag{2}$$

From Eqs. (1) and (2) it follows that

$$\log p = -\frac{L_0}{RT} + \frac{1}{R}\int^T \frac{\int_0^T C_p dT}{T^2} dT - \frac{1}{R}\int^T \frac{\int_0^T c_p dT}{T^2} dT + i, \tag{3}$$

where i is an integration constant, which varies only with the composition of the substance.

The quantum theory of specific heats, as developed by Debye and others, makes it possible to calculate the actual values of these integrals with a very satisfactory degree of accuracy for a large number of substances in the solid or gaseous states as the case may be.

O. Sackur [1] first showed that in the case of monatomic vapors the integration constant i could be expressed in terms of a *universal constant* i_0 and the molecular weight, by means of the relation

$$i = i_0 + 3/2 \log M, \tag{4}$$

where M is the molecular weight.

This conclusion has been subsequently confirmed by other investigators on the basis of dimensional considerations.[2]

At very low temperatures, it has been shown that the integral involving c_p becomes negligibly small. On the other hand, the specific heat of a monatomic gas at constant pressure is constant down to the lowest temperatures and is equal to $5/2\ R$. Consequently, under these conditions, Eq. (3) assumes the very simple form

$$\log p = -L_0/RT + 5/2 \log T + i_0 + 3/2 \log M. \tag{5}$$

Application to electron emission.—Now let us consider a metal in equilibrium with an electron atmosphere; also let us assume that the electron density in the space is so small that mutual repulsions may be neglected. We may then consider the evaporation of electrons from a metal as thermodynamically equivalent to the evaporation of a monatomic gas, for the electrons in the space necessarily have the same specific heat as the molecules of a monatomic gas. Now, experimental evidence shows that as a first approximation we may consider that the

[1] Ann. der Phys. **36**, 598 (1911); **40**, 67 (1913).

[2] R. C. Tolman, J. Am. Chem. Soc. **42**, 1185 (1920); **43**, 866 (1921).

electrons do not contribute to the specific heat of the metal. That is, with the possible exception of metals at extremely high temperatures, the specific heat of free electrons in the metal is zero. Hence, c_p is zero and Eq. (5) must also apply to the case of emission of electrons.

We may write this equation in the form

$$p = N^{3/2}m^{3/2}\epsilon^{i_0}T^{5/2}\epsilon^{-L_0/RT}, \tag{6}$$

where N = Avogadro's constant = 6.06×10^{23} and m = mass of an electron = 8.995×10^{-28} gm.

Now, according to the kinetic theory of gases, the number of electrons n striking the cathode per unit area in unit time is given by the relation $n = p/\sqrt{2\pi mkT}$, where k = Boltzmann's constant = 1.372×10^{-16} ergs/deg.

Since the electron atmosphere is in equilibrium with the hot metal, it follows that the number of electrons emitted must be equal to the number impinging if we assume that there is no reflection of electrons at the surface. Hence, the current per unit area per unit time is given by $I = ne = pe/\sqrt{2\pi mkT}$, where e = charge on electron.

Combining this with Eq. (6),

$$I = \left(\frac{N^{3/2}me\epsilon^{i_0}}{\sqrt{2\pi k}}\right)T^2\epsilon^{-b_0/T}, \tag{7}$$

where $b_0 = L_0/R$, corresponding to b in Richardson's equation for electron emission.

It is evident that the expression in the brackets is a *universal constant*. Denoting this by A, it follows that the electron emission for any substance can be expressed as a function of the temperature by an equation of the form

$$I = AT^2\epsilon^{-b_0/T}, \tag{8}$$

where b_0 is the only quantity that varies for different substances.

The value of the universal constant *A*.—(1) According to Sackur [1] and Tetrode, [2] the value of the chemical constant i_0 is given by the relation

$$i_0 = \log\left[\frac{(2\pi)^{3/2}k^{5/2}}{N^{3/2}h^3}\right]. \tag{9}$$

Substituting in Eq. (7), we therefore obtain the following equation for the electron emission as a function of the temperature:

$$I = ne = \left(\frac{2\pi k^2me}{h^3}\right)T^2\epsilon^{-b_0/T}, \tag{10a}$$

where the expression in the brackets corresponds to A in Eq. (8).

[1] Ann. der Phys. **36**, 598 (1911); **40**, 67 (1913).

[2] Ann. der Phys. **38**, 434 (1912).

Using the values $k = 1.372 \times 10^{-16}$ ergs/deg., $m = 8.995 \times 10^{-28}$ gm, $h = 6.55 \times 10^{-27}$ erg/sec,

$$A = 1.80 \times 10^{11} \text{ e.s.u./cm}^2 \text{ deg.}^2 = 60.2 \text{ amp./cm}^2 \text{ deg.}^2. \quad (10b)$$

(2) In 1914, G. N. Lewis and E. Q. Adams [1] developed a theory of ultimate rational units according to which the quantum constant is connected with the elementary unit charge by a simple numerical relation. More recently G. N. Lewis, G. E. Gibson and W. M. Latimer [2] have applied the same considerations in order to calculate the entropies of the elements. It can be shown that on the basis of their theory

$$A = \frac{k^2c^3m\epsilon^{5/2}}{(4\pi)^6e^5\sqrt{2\pi}} = \frac{2^{5/2}\pi^{9/2}\epsilon^{-5/2}}{15} \cdot \frac{kme}{h^3} \quad (11)$$
$$= 1.53 \times 10^{11} \text{ e.s.u./cm}^2 \text{ deg.}^2$$
$$= 51.2 \text{ amp./cm}^2 \text{ deg.}^2.$$

At the present stage, it is not possible on the basis of available vapor pressure data to decide definitely in favor of either of these values of A. On the one hand, it has been shown by A. C. Egerton [3] that the observations on the vapor pressures of zinc, cadmium, mercury and argon are in very good accord with the Sackur-Tetrode value of i_0, and similar results have been obtained by W. Nernst.[4] On the other hand, Lewis and his associates have made very careful calculations, based on experimental data, of the entropies of the four elements, helium, argon, cadmium and mercury, and find that in no case does the difference between the value of i_0 observed and that calculated on the basis of their theory exceed the probable experimental error.

Part II. Historical and Critical Remarks on the General Equation for Electron Emission

The generally accepted equation for electron emission is that first enunciated by O. W. Richardson, according to which

$$I = A_1\sqrt{T}\epsilon^{-b/T}. \quad (12)$$

In this equation A_1 and b are constants for any one substance. As pointed out by Richardson, b corresponds to L/R, where L is the latent heat of evaporation of the electrons. While the theoretical considerations on which the equation is based have not been considered quite satisfactory, the experimentally observed data on electron emission have actually been found to be in good agreement with the equation.

[1] Lewis and Adams, Phys. Rev. **3**, 92 (1914).
[2] Lewis, Gibson and Latimer, J. Am. Chem. Soc. **44**, 1008 (1922).
[3] Egerton, Phil. Mag. **39**, 1 (1920).
[4] Nernst, Grundlagen des neuen Wärme-Satzes, Chap. 13 (1918).

That Richardson himself has not been altogether satisfied with the validity of this equation is evident from the fact that he has also suggested an equation similar in form to Eq. (8) above. In his book on "The Emission of Electricity from Hot Bodies," [1] he pointed out that an equation of this form could be derived on the basis of the quantum theory. In the derivation of the value of A, he applied certain hypotheses which had been utilized by Debye and Keesom in calculating specific heats at low temperatures, and obtained a value which corresponds to 5 amp. cm^{-2} $deg.^{-2}$ instead of 60.2 (or 51.2) as calculated in Part I. of this paper.

J. Eggert [2] pointed out that the Nernst Heat Theorem could be applied to calculate the degree of ionization of various metals at the extremely high temperatures which exist in fixed stars, and utilized for this calculation Eq. (6), p referring, obviously, to the pressure of the ions (or electrons) produced by dissociation of the metal atoms, and L_0 to the energy necessary for dissociation into positive ion and electron.

The same relations were also applied by Megh Nad Saha [3] to calculate the ionization in the solar chromosphere.

The bearing of Eq. (3) on the problem of electron emission from metals has been discussed very recently by both Tolman [4] and Laue.[5] Tolman's argument is briefly as follows. For the evaporation of a monatomic gas from a solid, the following entropy relation has been shown to be valid:

$$S = 5/2\, R \log T - R \log P + S_1 + 3/2\, R \log M. \qquad (13)$$

In this equation S denotes the entropy at temperature T, P is the vapor pressure, S_1 is a constant for all monatomic gases and M denotes the molecular (or atomic) weight.

Tolman points out that while S_1 may be calculated on the basis of the equation derived by Sackur and Tetrode for i_0, there is still some doubt as to the validity of their arguments, and therefore he prefers to use the value calculated by Lewis and Gibson [6] from experimental data for helium.

According to this calculation, the value of the entropy for He at 298° K and 1 atmosphere pressure is 29.2. Hence,

$$S_1 = 29.2 - 3/2 \log 3.99 + 4.97 \log T - 1.987 \log (1.013 \times 10^6) = 24.21.$$

[1] Second Edition, pp. 37–41; also Phil. Mag. **28**, 633 (1914).
[2] Phys. Zeits. **20**, 570 (1919).
[3] Phil. Mag. **40**, 472 (1920).
[4] R. C. Tolman, J. Am. Chem. Soc. **43**, 1592 (1921).
[5] M. V. Laue, Jahrb. d. Elektronik u. Rad. **15**, 205, 257 (1918).
[6] J. Am. Chem. Soc. **39**, 2554 (1917), also R. C. Tolman, ib. **42**, 1185 (1920).

Tolman assumes now that electron emission is a phenomenon perfectly analogous to that of the evaporation of a monatomic substance, and that therefore Eq. (13) must also apply to this case. He calculates the pressure p of the electrons in equilibrium with the metal from the emission I. Substituting this value in Eq. (13) leads immediately to a value for S, the entropy at the temperature corresponding to the observed emission. From Langmuir's experimental data on the electron emission from tungsten, tantalum, and molybdenum at $T = 2000$, the values of S given in the fourth column of Table I. are obtained.

But $S = (F\phi + RT)/T$, where ϕ denotes the equivalent potential drop which the electrons have to overcome in escaping from the surface of the metal at the temperature T, and F denotes the Faraday constant. It is therefore possible also to calculate S from the observed value of ϕ. These have been determined by Lester [1] for the above metals and are given in the second column of Table I. The values of S calculated on this basis are given in the third column of the table.

Still another check on the value of S may be obtained by means of the fundamental equation (1) combined with Richardson's equation. On this basis,

$$S = \frac{L}{T} = RT \cdot \frac{d \log p}{dT} = RT \cdot \frac{d \log (I/\sqrt{T})}{dT}.$$

That is, S can be calculated from the rate of change of the electron emission with temperature. The values of S thus obtained are given in the last column.

TABLE I

	ϕ	S (from ϕ)	S (from I)	S (from slope)
Tungsten.....	4.478	53.6	53.3	54.1
Tantalum.....	4.511	54.0	52.3	51.6
Molybdenum.....	4.588	54.9	51.0	51.6

The agreement between the values of the entropy calculated by the different methods leads to the conclusion that the assumptions involved in the application of Eqs. (3) or (13) to electron emission are justifiable. The exact nature of these assumptions has been discussed rather fully by Tolman and also by Laue, so that consideration of this phase of the problem may be omitted in the present connection.

Relation between entropy constant, chemical constant and A in Eq. (8).—It is well in this connection to state briefly the relation between the constant S_1 used by these investigators and the chemical constant i_0

[1] Lester, Phil. Mag. **31**, 197 (1916).

introduced in the first part of this paper. This relation is easily derived from the following considerations:

For the evaporation of electrons at the temperature T, it has been shown above that Eq. (2) reduces to $L = L_0 + C_pT$. Therefore,

$$S = L/T = L_0/T + C_p.$$

Substituting for S in Eq. (13) and comparing this with Eq. (5), we obtain the relation

$$i_0 = (S_1 - C_p)/R. \tag{14}$$

By means of this equation combined with Eq. (7) it is therefore possible to calculate the constant A for any given value of S_1.

It is usual in discussions of vapor pressure data to replace the constant i_0 by $C_0 = i_0/2.303$, since this makes it possible to use ordinary logarithms. As this latter constant is the one usually given in most publications on this subject, it has been considered worth while to tabulate for reference the corresponding values of C_0, S_1, and A based on the theories of Sackur and Tetrode on the one hand and of Lewis and his associates on the other. The value of S_1 used by Tolman and the corresponding value of A are also given for comparison.

	S_1	$C_0 = i_0/2.303$	A (amp./cm² deg.²)
Sackur-Tetrode	25.19	− 1.5877*	60.24
		4.4178†	
Lewis	24.87	4.354†	51.2
Tolman	24.27		38.4

* Pressure in atm.

† Pressure in bars.

Accuracy of determination of A from electron emission data.—In view of the relation between the value of A and that of S_1 (or C_0) it would appear at first glance as if evidence in favor of one theory or the other might be obtained from electron emission data.

From Eq. (8) it follows that

$$b_0 = \frac{\Delta \log (I/T^2)}{\Delta(1/T)}. \tag{15}$$

Consequently it is possible to derive a value for b_0 independently of any assumed value of A, by plotting $\log (I/T^2)$ against $1/T$ and noting the slope of the resulting straight line. From this value of b_0, that of A may then be obtained by direct substitution in Eq. (8).

The difficulty, however, in using this method to determine the value of A, arises from the very form of the above equation, where b_0 and T

both enter into the exponential factor, while A is a coefficient of this factor.[1] Hence, the slightest error in the determination of either b_0 or T leads to a considerably greater error in the resulting value of A.

Thus for the case $T = 2000$, and $b_0 = 50{,}000$, it can be shown that an error of one per cent in b_0 produces an error of 25 per cent in that of A. Hence, to attain a sufficiently high degree of accuracy in the determination of A, for the present purpose, it would be necessary to obtain values of b_0 accurate to at least 0.25 per cent.

The accuracy of temperature determination varies for different metals. In the case of tungsten, for which as a result of the work of Langmuir, and of Worthing and Forsythe, the temperature scale is most accurately known, it is possible to measure temperatures in the range 1500–2500° K with an accuracy of 5 degrees. This is, nevertheless, not exact enough to settle the question as to the most satisfactory value of A.

While the theory advanced by Lewis and his associates must be regarded as much more reasonable than that postulated by Sackur and Tetrode, it has been found in the case of tungsten that with the temperature scale used by Worthing and Forsythe, the observed electron emission data are in somewhat better agreement with the value $A = 60.24$ amp./cm^2 deg.^{2}. It is, however, obvious, as a consequence of the considerations mentioned above, that this result cannot be regarded as a direct confirmation of the Sackur-Tetrode theory. For the present purposes, we must merely regard the value of A given above as one which is in satisfactory agreement with the standard temperature scale for tungsten. It is, therefore, the value which will be adopted in this paper and in subsequent ones on electron emission.

Application of the equation for electron emission to the determination of true temperatures.—The equation for electron emission, as derived on the basis of the considerations stated in the previous section, can be expressed in a form which is much more convenient for calculation as follows:

$$\log_{10} (I/T^2) = 1.7792 - b_0/2.303T, \tag{16}$$

where I = emission in amp./cm^2 at the temperature T.

There is an interesting application of this equation which ought to be pointed out in this connection. It is evident that at any given temperature T, the emissions I' and I'' for two different substances are connected with the corresponding values b_0' and b_0'' by the relation

$$\log_{10} I'' - \log_{10} I' = (b_0' - b_0'')/2.303T. \tag{17}$$

Thus, given any substance for which b_0' is known, it is possible to

[1] This has also been pointed out by Richardson, loc. cit., p. 86.

determine b_0'' for the other substance by enclosing the two in a "Hohlraum" ("black body" enclosure) and measuring the relative emissions. For this purpose it is not at all necessary to know the temperature of the enclosure. The value of T in the above equation is determined from the observed value of log I and the corresponding value of b_0. Once b_0' is determined by this method for the second material, it is obviously possible, by going back to Eq. (16), to determine a true temperature scale for this material. That the electron emission may be used to measure temperatures has been pointed out by Richardson and others. However, this method is not so directly applicable if Richardson's equation is adhered to, since this involves also a knowledge of the integration constant A in the latter equation, whereas assuming the validity of Eq. (8), the determination of a true temperature scale for any substance becomes a much simpler matter.

Thermionic work function.—In the derivation of Eq. (8), $b_0 = L_0/R$. This constant is related to the thermionic work function ϕ_0, at the absolute zero, by the relations

$$\phi_0 = L_0/Ne = Rb_0/Ne = kb_0/e = 8.62 \times 10^{-5} b_0 \text{ volts.} \qquad (18)$$

Denoting the work function corresponding to b in Richardson's equation by ϕ, it follows that

$$\phi = \phi_0 + \frac{3}{2}\frac{k}{e}T \qquad (19)$$

and

$$b = b_0 + \frac{3}{2}T. \qquad (20)$$

A number of investigators have attempted to measure ϕ directly by observations on the cooling effect produced by the evaporation of the electrons. In a previous connection, mention has been made of Lester's measurements in the case of several metals. The most recent contribution on this subject is by C. Davisson and L. H. Germer [1] who made some extremely accurate observations in the case of tungsten. It is of interest to point out the relation between the experimental data obtained by such measurements and the values of ϕ_0 as determined from emission data at different temperature.

If we assume that the electrons in the metal do not possess any thermal energy of agitation, and denote the observed cooling effect at the temperature T by P (in volts), it can be deduced from simple considerations that

$$Pe = \phi_0 e + 2kT. \qquad (20)$$

[1] Phys. Rev. **20**, 300 (1922).

That is, the energy absorbed per electron leaving the surface is equal to the work done against electrical forces (see subsequent portion of this paper) plus the kinetic energy of the emitted electrons. As shown by Richardson,[1] the average kinetic energy of the emitted electrons is $2kT$ and not $3/2\,kT$.

Davisson and Germer find that in the case of the electron emission from tungsten, ϕ_0 as derived from calorimetric determinations (*i.e.*, by means of Eq. (20)) is 4.52 volts, whereas direct measurement of the emission as function of temperature leads to the value 4.48 volts. The agreement between the two values may be regarded as very satisfactory, as it is well within the limits of experimental errors.

Part III. Experimental Results

In a series of subsequent papers, experimental data will be given to demonstrate the validity of the equations deduced in this paper, over a large range of temperatures, for several different metals. However, the electron emission data on tungsten recently published by Davisson and Germer[2] serve as a confirmation of the validity of Eq. (10) by independent observers.

These data are given in the first and third columns of Table II. The first column gives the value of T on the basis of the scale used by Worthing and Forsythe, while the fourth column gives the values of $\log_{10} I$, where I denotes the electron emission in amperes per cm², as calculated from the values observed for a filament of area 0.1825 cm². The observed emissions are given in the third column. From these data the values of b_0 given in the sixth column were calculated by means of Eq. (10). The average of these values is 51,860.

Fig. 1 shows the values of $\log_{10}(I/T^2)$ plotted against $1/T$. As has been pointed out in Part I., a satisfactory test of the validity of Eq. (8) or (10) is obtained when the value of b_0 calculated from the slope $\Delta \log_{10}(I/T^2)/\Delta(1/T)$ is found to be in agreement with the values of b_0 calculated from the emission data at different temperatures. The slope of the straight line drawn through the points in Fig. 1 is actually observed to be identical with the average value of b_0 given in Table II.

Such a test has also been applied to data published by W. Schlichter on the electron emission from platinum and nickel.[3]

Table III. gives the values of b_0 calculated from the emission data for platinum. It will be observed that the greatest deviation from the aver-

[1] Loc. cit., p. 156.
[2] Loc. cit.
[3] Ann. der Phys. **47**, 573 (1915).

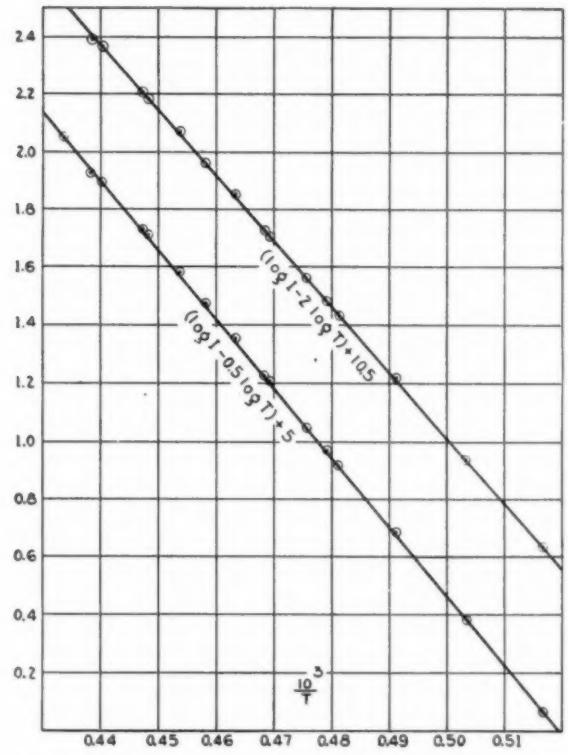

Fig. 1. Plot of emission data for tungsten obtained by Davisson and Germer.

TABLE II

Electron Emission Data for Tungsten Filament (Area = 0.1825 cm²) Obtained by Davisson and Germer *

T	$\frac{10^3}{T}$	$i \times 10^3$	$\log I + 4$	$\log I - 2 \log T + 10$	b_0	$\log I - 0.5 \log T + 5$
1935.5	0.5167	0.0934	0.7091	0.1355	51,890	0.0658
1986.5	.5034	0.1973	1.0340	0.4378	51,880	0.3850
2036.0	.4912	0.3967	1.3373	0.7197	51,860	0.6829
2077.5	.4813	0.6784	1.5703	0.9351	51,880	0.9116
2086.5	.4793	0.7656	1.6228	0.9838	51,900	0.9631
2102.0	.4758	0.9363	1.7102	1.0650	51,840	1.0489
2131.5	.4692	1.362	1.8729	1.2155	51,840	1.2086
2134.5	.4685	1.419	1.8907	1.2321	51,870	1.2261
2158.0	.4634	1.902	2.0180	1.3500	51,820	1.3510
2182.0	.4583	2.538	2.1433	1.4655	51,810	1.4739
2204.0	.4537	3.269	2.2532	1.5668	51,820	1.5816
2231.0	.4482	4.405	2.3828	1.6858	51,820	1.7086
2235.0	.4474	4.606	2.4022	1.7036	51,870	1.7276
2271.5	.4402	6.875	2.5761	1.8635	51,880	1.8980
2280.0	.4386	7.394	2.6076	1.8918	51,920	1.9287
2306.0	.4337	9.792	2.7297	2.0041	51,900	2.0483
					Avg. 51,860	

* Ordinary $\log_{10}$ are used in this table.

age value 49,250 is about one half per cent. The same value is obtained from the slope directly. In the case of nickel, the average value of b_0 calculated from the emission data is 47,800, and the value obtained from the slope is 48,000.

TABLE III

Schlichter's Data on Emission from Platinum (Area = 23 cm²)

T	$i \times 10^3$ (amp.)	b_0
1211	0.42	49,300
1243	1.35	49,200
1275	4.17	49,100
1307	9.9	49,300
1339	27.5	49,200
1371	76	49,000
1403	168	49,100
1435	400	49,100
1467	785	49,300
1499	1430	49,500
		Avg. 49,250

While these results and numerous observations by the writer and his associates thus show satisfactory agreement with the deductions based on Eq. (8), it is however only just to point out that all these observations are equally well represented by an empirical equation involving $T^{1/2}$ instead of T^2. Richardson and other observers have in fact noted that within the limits of experimental error it is impossible to show by plotting either $\log_{10}(I/T^2)$ or $\log_{10}(I/\sqrt{T})$ against $1/T$ that either set of data gives a better straight line.

Table II. gives in the last column values of $\log_{10}(I/\sqrt{T})$ calculated from Davisson and Germer's observations. As is evident from Fig. 1, the plot of these data is a straight line, which differs only in the value of the slope ($b_0 = 55{,}410$) from the plot of $\log_{10}(I/T^2)$. The reason for this lack of any difference between the plots is the practical impossibility of measuring emission data over an extremely wide range of temperatures. Thus, in the case of tungsten, over a temperature range from 1000° K to 2500° K, the emission increases in the ratio 10^{15} approximately, while the ratio of values of $T^{1/2}$ is 1.58 and of T^2, 6.25.

The advantages in the equation derived in the present paper lie firstly in the theory underlying its derivation and secondly in the conclusion that the integration constant A is the same for all metals. Consequently it is possible to determine b_0 for any substance by measuring its emission at *only one temperature* instead of at two or more.

The values of b_0 obtained for a number of metals are given in Table

IV.[1] In the case of tungsten and that of thorium (obtained from thoriated tungsten filaments), the values are accurate to about one half per cent, while in the case of molybdenum and that of tantalum the degree of accuracy is probably one per cent. This is largely due to lack of very accurate temperature data for these metals. The emission for uranium, zirconium, yttrium, and cerium was measured on tungsten filaments containing additions of these elements as oxides (in a manner similar to that in which thoria is added to tungsten). It is not certain that in all these cases the maximum emission observed corresponded to that of a surface completely covered with a layer one atom deep of the added element, as the latter are much more volatile than thorium under similar conditions. Hence, the values of b_0 obtained for these elements must be regarded as upper limits.

The value of b_0 for calcium corresponds to the maximum emission observed when evaporating the metal in a vacuum and allowing it to condense on a tungsten surface.

The third column of Table IV. gives the corresponding values of ϕ_0. Schottky [2] and subsequently Langmuir [3] applied the theory of electrical images to calculate the distance x_0 at which the electron leaving the metal ceases to be attracted by the charge induced on the surface. According to this theory, $\phi_0 = e/2x_0$.

Converting to volts

$$x_0 = 7.16 \times 10^{-8}/\phi_0 \text{ cm.} \qquad (22)$$

Now it is reasonable to expect that this distance should be less than the molecular diameter σ, and that the ratio x_0/σ should be greater the more electropositive the element.[3] The value of σ can be calculated from the atomic volume V by the relation

$$\sigma = 1.33 \times 10^{-8} V^{1/3}. \qquad (23)$$

Table IV. gives the values of x_0, σ and x_0/σ calculated by means of these equations for the different elements.

One point that seems to be well established by these results is that the value of b_0 (or ϕ_0) is just as specific a constant for each element as its ordinary latent heat of evaporation. On the basis of some measurements of ϕ obtained by Lester for the elements molybdenum, carbon, tungsten,

[1] The observations in the case of W, Th, Mo, Ta and Ca were made in conjunction with Mr. H. N. Rowe and Mr. C. A. Kidner, while those on Zr, Yt, Ce and U were made by Mr. D. M. Dennison. The emission data on which the values of b_0 are based will be published in subsequent papers.

[2] Schottky, Phys. Zeits. **15**, 872 (1914).

[3] Langmuir, Trans. Am. Electrochem. Soc. **29**, 125 (1916).

and tantalum, Richardson has suggested that the work functions might be found to be the same for all substances.[1] The data in Table IV. and reliable data on the values of ϕ for different oxides published in Richardson's book, however, show definitely that the above suggestion is quite untenable.

TABLE IV

Values of b_0, ϕ_0, Etc., for Different Metals

Metal	b_0	ϕ_0	$x_0 \times 10^8$	$\sigma \times 10^8$	x_0/σ	N
Calcium.....	26,000	2.24	3.19	3.95	0.81	20
Yttrium.....	37,000	3.19	2.25	3.80	0.59	39
Zirconium.....	38,000	3.28	2.19	3.22	0.68	40
Molybdenum ..	50,000	4.31	1.66	2.93	0.57	42
Cerium.....	35,600	3.07	2.33	3.63	0.64	58
Tantalum.....	51,000	4.31	1.66	2.95	0.56	73
Tungsten.....	52,600	4.53	1.58	2.81	0.56	74
Thorium.....	34,100	2.94	2.44	3.68	0.66	90
Uranium.....	38,000	3.28	2.19	3.10	0.70	92

It is, of course, of interest to determine, if possible, the relation between b_0 for any element and other properties of this element. The results obtained so far, however, are insufficient to be more than suggestive. It is evident that b_0 (or ϕ_0) is lower, the greater the atomic volume (or atomic diameter). Also, apparently x_0/σ is a periodic property of the atomic number N with a maximum value which tends to approach 1 for the alkali and alkaline earth elements, while for elements of group VI. (tungsten, molybdenum, and uranium), the value of this ratio is a minimum. Further investigations on the electron emission from other metals must be carried out before any definite theory on this subject can be formulated.

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SCHENECTADY, N. Y.,
January 4, 1923

[1] Loc. cit. p. 189.

THE SCATTERING OF ELECTRONS BY A POSITIVE NUCLEUS OF LIMITED FIELD

By C. Davisson

Abstract

Theory of the angular distribution of electrons scattered by a positive nucleus of limited field.—(1) *Simple theory.* It is shown that if a random distribution of electrons moving on parallel lines with a common velocity, corresponding to V volts, is projected into a central field of force given by E/r^2 for values of $r < \rho$, and by zero for $r > \rho$, the intensity of scattering in a direction making an angle Ψ with the incident beam will be proportional to $[(2\mu - 1)/[(2\mu - 1)^2(1 + \cos \Psi) + (1 - \cos \Psi)]]^2$, where $\mu = V\rho/E$, provided the variation in mass of the electron with speed is disregarded. (2) *Allowing for variation of mass of the electrons with speed* so that the trajectories of the electrons through the limited field conform to the orbits calculated by C. G. Darwin, the distribution patterns will depart considerably from those calculated on the simple theory, particularly for small values of V. Semi-graphical methods are developed for constructing the distribution curves when V, ρ, and E are given. (3) *Taking into account the mutual energy of electron and nucleus* according to the view suggested recently by H. A. Wilson, the actual scattering patterns may be expected to conform closely to those calculated on the simple theory.

THE experiments of Geiger and Marsden[1] established the important fact that the angular distribution of α-particles scattered by various metals is in accord with the single scattering theory developed by Rutherford.[2] On this theory the positive charge of the atom is concentrated in an exceedingly small nucleus at the center of the atom structure, and the field about this nucleus is central with an intensity given by E/r^2, where E represents the nuclear charge, and r the distance from its center. Further experiments by Chadwick[3] established what had already been suggested by Geiger and Marsden's results, that E is given by Ne, where N represents the atomic number of the scattering metal, and e the elementary electron charge. It was also shown from the data of these experiments that in the case of gold and platinum the inverse square law of force must hold quite accurately between the limits $r = 3 \times 10^{-12}$ cm and $r = 4 \times 10^{-11}$ cm. These limits correspond respectively to the nearest approach of the α-particle to the nucleus in a head-on collision, and to the distance between the nucleus and the

[1] Geiger and Marsden, Proc. Roy. Soc. A **82**, 495 (1909); A **83**, 492 (1910); Phil. Mag. **25**, 604, 1913.

[2] Rutherford, Phil. Mag. **21**, 669 (1911); **22**, 488 (1914).

[3] Chadwick, Phil. Mag. **40**, 745 (1920).

line of approach of an α-particle which suffers the least measurable deflection.

In the theory referred to it is assumed that the field about the nucleus is unlimited, that is, that its intensity is given by E/r^2 for all values of r. This is permissible in the case considered on account of the great energy of the α-particles. All appreciable deflections occur so close to the nucleus that the nature of the field beyond $r = 10^{-10}$ cm is entirely unimportant. It is unnecessary, therefore, to take into account the effect on the field of the structural electrons as these lie outside this limit. Or, to state the case more accurately, the agreement between the calculated and observed distributions of scattering is evidence that the structural or orbital electrons in the atoms investigated do lie outside this limit.

It is evident, however, that the assumption of an unlimited field, even for purposes of calculation, will not in general be permissible in considering the scattering of β-particles and more slowly moving electrons. The energy of even the most swiftly moving β-particles is small compared with that of α-particles, and appreciable deflections would occur in an unlimited field at distances from the nucleus which are greater than the distances to the nearest electrons. It is to be expected then that departures from the inverse square field arising from the shielding action of these electrons will give rise to corresponding departures from the distribution of scattering observed in the case of α-particles. Such departures have been observed recently by Schonland [1] in the distribution of β-particles scattered by various metals and have been ascribed to this action. In the case of slow moving electrons the writer and Dr. C. H. Kunsman [2] have published preliminary results for nickel which show that the angular distribution of scattering is so greatly affected by the outlying electrons in the atom that it bears no resemblance whatever to that deduced by Rutherford for α-particles.

What we require then for the proper interpretation of electron scattering is a calculation similar to Rutherford's for α-particles, but modified to allow for the shielding action of the structural electrons. As a first step it may be assumed that the field intensity about the nucleus is given by E/r^2 for values of r less than a particular value ρ, and that for all values of r greater than ρ the intensity is zero. This is the case treated in this paper. While these field conditions are doubtless much simpler than those obtaining in any atom, it nevertheless appears from further experimental results which we shall publish in the near future that they

[1] Schonland, Proc. Roy. Soc. A **101**, 299 (July, 1922).

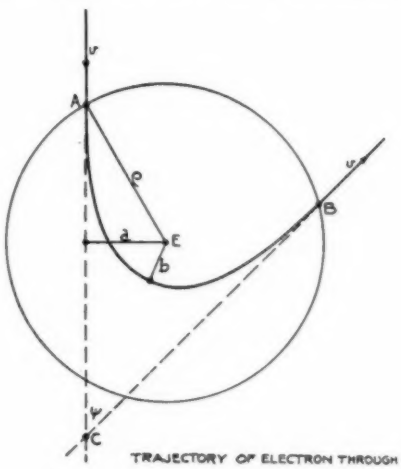
[2] Davisson and Kunsman, Science, **54**, 1404, 522 (Nov. 25, 1921).

sufficiently represent conditions in some of the lighter atoms, such as magnesium and aluminium, to account for the main features exhibited by the scattering of low speed electrons by these elements.

The calculation is carried through in the first instance without regard to the variation of mass of the electrons with speed. The most striking results are that the angular distribution of scattering is a function of a single parameter $\mu = V\rho/E$, where V is the potential drop through which the electrons acquire their incident speed, and that for values of μ less than unity the maximum intensity of scattering is in the direction opposite to that of the motion of the electrons in the incident beam. The variation in mass of the electron with speed is then considered, and it is found that when this is allowed for the distribution depends upon V as well as upon μ. It has not been found possible in this case to arrive at an explicit formula for the intensity of scattering as a function of μ and V, but semigraphical methods are developed for constructing the distribution curve for any pair of values of these quantities.

The Simple Theory

An electron moving downward in Fig. 1 with velocity v enters the field of the positive charge E at the point A, executes a portion of a conic orbit in this field and emerges at the point B. We first require an expression for the angle Ψ between the two straight branches of the trajectory.



TRAJECTORY OF ELECTRON THROUGH LIMITED INVERSE SQUARE FIELD

Fig. 1

If d and b represent the distances from E to the line of approach of the electron, and to the apse of the orbit respectively, then by the equal areas theorem, $vd = v_0 b$, where v_0 is the apsoidal velocity.

From energy considerations $\frac{1}{2}m(v_0^2 - v^2) = eE(1/b - 1/\rho)$. Elimination of v_0 between these equations gives

$$\tfrac{1}{2}mv^2(d^2/b^2 - 1) = Ve(d^2/b^2 - 1) = Ee(1/b - 1/\rho),$$

where V represents the potential drop through which the electron acquired its incident velocity. Solving this equation for b, we obtain

$$b = \frac{\dfrac{2d^2V}{E}}{1 \pm \left[1 + 4\dfrac{d^2V^2}{E^2}\left(1 - \dfrac{E}{V\rho}\right)\right]^{1/2}}.$$

The two values of b are the distances from E to the apses of the two branches of the trajectory, in the case of hyperbolic orbits, or the distances from E to the extremities of the major axis, in the case of elliptic orbits. If the equation of the orbit in polar coördinates is $r = p/(1 + \epsilon \cos \Theta')$, these same distances are given by $b = p/(1 \pm \epsilon)$. We have, therefore, for the constants of the orbit

$$p = 2\frac{d^2V}{E} \quad \text{and} \quad \epsilon = \left[1 + \frac{4d^2V^2}{E^2}\left(1 - \frac{E}{V\rho}\right)\right]^{1/2}.$$

If Θ represents the value of Θ' for the electron at A, and α represents the angle EAC (Fig. 1), then $\frac{1}{2}\Psi + \alpha + \Theta = \pi$, and $\cos \frac{1}{2}\Psi = \sin \alpha \sin \Theta - \cos \alpha \cos \Theta$. Now $\rho = p/(1 + \epsilon \cos \Theta)$, so that

$$\cos \Theta = \frac{1}{\epsilon}\left(\frac{p}{\rho} - 1\right) \quad \text{and} \quad \sin \Theta = \frac{1}{\epsilon}\left[\epsilon^2 - \left(\frac{p}{\rho} - 1\right)^2\right]^{1/2}.$$

Also $\sin \alpha = d/\rho$ and $\cos \alpha = (\rho^2 - d^2)^{1/2}/\rho$. Substituting these values into the equation for $\cos \Psi/2$,

$$\cos \Psi/2 = (1/\epsilon\rho)[d(\epsilon^2 - (p/\rho - 1)^2)^{1/2} - (p/\rho - 1)(\rho^2 - d^2)^{1/2}].$$

Combining the values found above for ϵ and p, we find $\epsilon^2 = 1 + p^2/d^2 - 2p/\rho$ so that $d(\epsilon^2 - (p/\rho - 1)^2)^{1/2} = (p/\rho)(\rho^2 - d^2)^{1/2}$ and the expression for $\cos \Psi/2$ becomes $\cos \Psi/2 = (\rho^2 - d^2)^{1/2}/\epsilon\rho$. We have then $\cos \Psi = 2 \cos^2 \frac{1}{2}\Psi - 1 = [(2 - \epsilon^2)\rho^2 - 2d^2]/\epsilon^2\rho^2$. Substituting for ϵ^2 and rearranging, we find [1]

$$\cos \Psi = \frac{(\rho^2 - d^2)E^2 - d^2(2V\rho - E)^2}{(\rho^2 - d^2)E^2 + d^2(2V\rho - E)^2}.$$

If the system here considered is under random bombardment by electrons of uniform speed incident along parallel lines, the number of electrons approaching the nucleus per second in the range $d \pm \frac{1}{2}\Delta d$

[1] An equivalent formula given recently by H. A. Wilson is referred to at the end of this article.

will be $dn = (2\pi Nd)\Delta d$, N representing the number of electrons passing per second through unit area at right angles to the incident beam. These will turn up after deflection in the angular interval $\Psi \pm \frac{1}{2}\Delta\Psi$ corresponding to the solid angle element $d\Omega = 2\pi \sin \Psi \, \Delta\Psi$. The intensity of scattering in the direction Ψ is, therefore,

$$I_\Psi = \frac{dn}{d\Omega} = N\frac{d \cdot \Delta d}{\sin \Psi \, \Delta\Psi} = -\frac{N}{2}\frac{\Delta d^2}{\Delta \cos \Psi}.$$

Solving the equation for $\cos \Psi$, for d^2 and differentiating this with respect to $\cos \Psi$ and substituting into the expression for I_Ψ, one obtains finally

$$I_\Psi = N\rho^2\left[\frac{(2\mu - 1)}{(2\mu - 1)^2(1 + \cos \Psi) + (1 - \cos \Psi)}\right]^2,$$

where μ has been written for the ratio $V\rho/E$. This is the formula given in a preliminary note [1] without derivation.

The distribution of scattering represented by this formula has the following properties:

(1) the distribution for $\mu = \frac{1}{2} + \lambda$ is the same as the distribution for $\mu = \frac{1}{2} - \lambda$. Negative values of μ, however, have no physical significance;
(2) for $\mu = \frac{1}{2}$, I_Ψ is infinite in the direction $\Psi = 0$ and zero in all other directions;
(3) for $\mu = 0$ and $\mu = 1$, I_Ψ is independent of Ψ, that is, the electrons are scattered uniformly in all directions;
(4) for $1 > \mu > 0$, the maximum I_Ψ is in the direction $\Psi = 0$;
(5) for $\mu > 1$, the maximum I_Ψ is in the direction $\Psi = \pi$;
(6) for ρ infinite, the equation reduces to a form equivalent to that representing α-ray scattering.

These properties are exhibited graphically, except the last, by the family of curves shown in Fig. 2.

It will be noted that $\mu = V\rho/E$ is the ratio of the kinetic energy of the electron as it enters the field to the kinetic energy it would have acquired in falling to this point from an infinite distance in an unlimited field.

An idea of the order of magnitudes of the quantities involved may be gained from the fact that if $E = n \times 4.774 \times 10^{-10}$ e.s.u. and $\rho = m \times 10^{-9}$ cm, then μ has the value unity when $V = 143 \times n/m$ volts.

[1] Davisson and Kunsman, Science, **54**, 1404, 522 (1921).

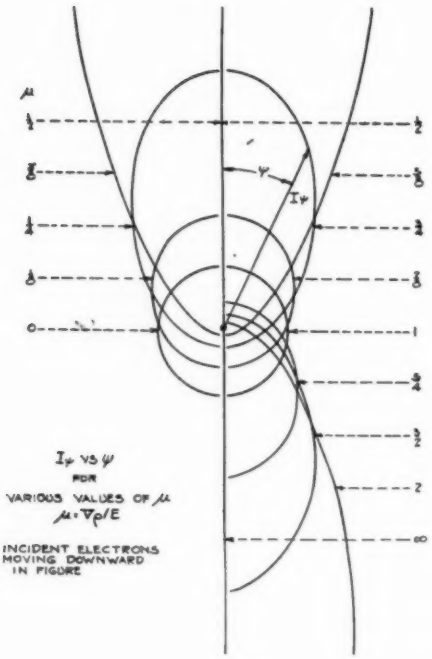


Fig. 2

Theory Based on Darwin's Orbits

We now consider to what extent the variation in mass of the electrons with speed may be expected to affect the distribution of scattered particles.

It has been shown by C. G. Darwin [1] that if the longitudinal and transverse masses of the electron are taken respectively as $m(1-v^2/c^2)^{-3/2}$ and $m(1-v^2/c^2)^{-1/2}$, the orbit of such an electron projected into the field of a positive nucleus will be given by

$$\frac{p}{r}\cot\mu\tan\chi\sin\chi=\cos\chi-\cos(\theta\cot\mu\tan\chi+\chi),$$

where p, r and θ represent respectively the distance from the nucleus to the line of approach of the electron, the radius vector, and the angle measured from the direction of approach of the electron as indicated in Fig. 3. χ and μ are constants of the orbit that may for the present be left undefined.

If in this equation we replace θ by $\theta'+\bar{\theta}$, where $\bar{\theta}$ is a constant, the value of $\bar{\theta}$ may be chosen to satisfy the condition: $\bar{\theta}\cot\mu\tan\chi+\chi=\pi$.

[1] Darwin, Phil. Mag. **25**, p. 201 (1913).

The equation then takes the form $r = p'/(1 + \epsilon' \cos \gamma \Theta')$, where γ has been written for $\cot \mu \cdot \tan \chi$. The value of γ as derived by Darwin is $[1 - (a^2/p^2) \cot^2 \bar{\beta}]^{1/2}$, where $a = Ee/mc^2$ and $\sin \bar{\beta} = \bar{v}/c$. E and e represent the charges of the nucleus and electron respectively, m the limiting mass of the electrons for low speeds, $\bar{v}$ the initial velocity of the electron at an infinite distance from E, and c the velocity of light.

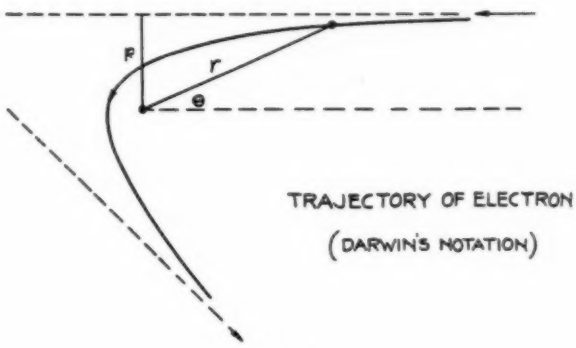


Fig. 3

Referring again to Fig. 1, we may carry through the argument as before, at least to a certain point. We have, now, to replace the approximate conditions of ordinary mechanics by the more general conditions of the relativity theory. The conservation of angular momentum now leads to the relation $\bar{v}p/\cos \beta = vd/\cos \beta = v_0 b/\cos \beta_0$, or $p \tan \bar{\beta} = d \tan \beta = b \tan \beta_0$, where β and β_0 correspond respectively to the velocities v and v_0. And the ordinary expression for the kinetic energy of the electron is replaced by K.E. $= mc^2(1/\cos \beta - 1)$. The conservation of energy then leads to the relation $mc^2(1/\cos \beta_0 - 1/\cos \beta) = Ee(1/b - 1/\rho)$. Eliminating β_0 between these equations and solving for b, we find

$$b = \frac{\dfrac{d^2 \tan^2 \beta - a^2}{a\left(\dfrac{1}{\cos \beta} - \dfrac{a}{\rho}\right)}}{1 \pm \left[1 + \left(1 - \dfrac{1}{\left(\dfrac{1}{\cos \beta} - \dfrac{a}{\rho}\right)^2}\right) \dfrac{d^2 \tan^2 \beta - a^2}{a^2}\right]^{1/2}}.$$

We also have from the general equation $b = p'/(1 + \epsilon')$. It does not follow immediately that the numerator of the first expression for b and the irrational quantity in its denominator are the values of p' and ϵ' respectively. We will assume, however, from analogy with the former case that they are these quantities, and proceed to reduce them to more

convenient form. The condition of constant angular momentum enables us to write $\gamma^2 = 1 - a^2/p^2 \cot^2 \beta = 1 - a^2/d^2 \cot^2 \beta$ from which we have $d^2 \tan^2 \beta - a^2 = d^2\gamma^2 \tan^2 \beta$, and $a = d(1 - \gamma^2)^{1/2} \tan \beta$. Also, since Ve is equal to the kinetic energy and $a = Ee/mc^2$, $Ve = (Ee/a)(\cos^{-1} \beta - 1)$ and $a = (E/V)(\cos^{-1} \beta - 1) = (\rho/\mu)(1 - \cos \beta)/\cos \beta$, where $\mu = V\rho/E$, as formerly. Writing this into the expression for γ^2, we have $\gamma^2 = 1 - (1/\mu^2\delta^2)(1 - \cos \beta)/(1 + \cos \beta)$, where $\delta = d/\rho$. When the expressions for p' and ϵ' appearing in the expression for b are transformed by means of these relations, we find that writing $\sigma = (1 - \cos \beta)$, $(1 + \cos \beta) = 2 - \sigma$, $p' = [\rho/(\mu - \sigma)][\mu^2(2 - \sigma)\delta^2 - \sigma]$ and

$$\epsilon' = \frac{\mu}{\mu - \sigma}[(\mu - 1)(2 - \sigma)(\mu(2 - \sigma) - \sigma)\delta^2 + (1 - \sigma)^2].$$

Setting σ equal to zero, these reduce to the values found for these quantities on the simple theory, as they should, for this amounts to regarding the velocity of light as infinite, and reducing the treatment to that of ordinary mechanics.

Returning again to the general equation for the orbit, we see that if $\Theta/2$ be used to represent the value of Θ' for the electron as it enters the field ($r = \rho$), then $\cos \gamma\, \Theta/2 = (1/\epsilon')(p'/\rho - 1)$ and

$$\cos \gamma\, \Theta = 2(1/\epsilon')^2(p'/\rho - 1)^2 - 1,$$

Θ being the total angle through which the radius vector turns while the electron remains in the field. Substituting into this the expression found for p' and ϵ', we find

$$\cos \gamma\, \Theta = \frac{2[1 - (2 - \sigma)\mu\delta^2]^2}{(1 - \sigma)^2 + (2 - \sigma)(\mu - 1)[\mu(2 - \sigma) - \sigma]\delta^2} - 1,$$

where

$$\gamma = \left[1 - \frac{\sigma}{(2 - \sigma)\mu^2\delta^2}\right]^{1/2}.$$

We have then the means of calculating Θ for any combination of values of μ, δ and σ. Since $Ve = mc^2\sigma/(1 - \sigma)$,

$$\sigma = \frac{Ve}{mc^2} \Big/ \left[1 + \frac{Ve}{mc^2}\right] = 1.96 \times 10^{-6}V/(1 + 1.96 \times 10^{-6}V)$$

for V in volts. Having determined Θ, the angle Ψ in which we are really interested can be calculated from $\Psi = 2\pi - (2\alpha + \Theta)$, where, as before, $\alpha = \sin^{-1} d/\rho = \sin^{-1} \delta$.

In connection with the simple theory it was found that

$$I_\Psi = -\frac{N}{2}\frac{\Delta d^2}{\Delta \cos \Psi}.$$

This is at once applicable to the present case and may be written

$$I_\Psi = -\frac{N\rho^2}{2}\frac{\Delta\delta^2}{\Delta\cos\Psi}.$$

Thus if we choose particular values of μ and σ, (V), values of $\cos\Psi$ can be found for a series of values of δ. Plotting then δ^2 against $\cos\Psi$, values of I_Ψ can be found from the slope of the resulting curve.

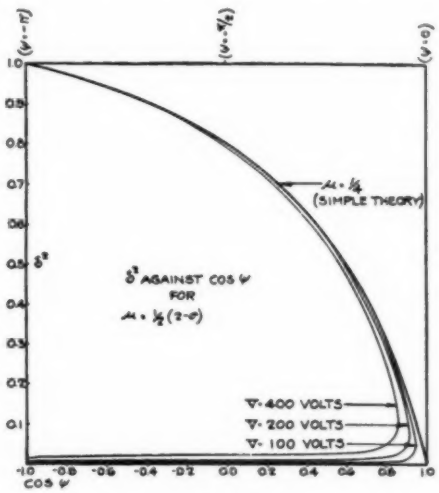


Fig. 4

In Fig. 4 curves of δ^2 against $\cos\Psi$ are shown for $\mu = \frac{1}{2}(2-\sigma)$, and a series of values of V. The heavy curve is the graph of δ^2 against $\cos\Psi$ on the simple theory for the corresponding value of μ, $(\mu = \frac{1}{4})$, and is independent of V. It will be noticed that as V increases, the distribution departs more and more from that calculated on the basis of ordinary mechanics. Starting with $\cos\Psi = -1$, $(\Psi = -\pi)$, the intensity is greater than on the simple theory, as indicated by the greater slope of the curve, for all values of Ψ back to a critical value, Ψ', depending upon V, where it becomes infinite. For lower values of δ^2 the curve turns back indicating a second group of particles scattered in the interval between Ψ' and $\Psi = -\pi$. The intensity of this scattering is much less, however, than that of the first group considered. That the slope of this second section of the curve is of opposite sign to the first is due to the fact that in this region Ψ decreases as δ decreases, whereas in the first section Ψ increased as δ decreased. The intensities are positive in both cases. The branch of the curve of which the "second section" is the beginning continues indefinitely and is asymptotic to $\delta^2 = \sigma/(2-\sigma)\mu^2$.

The electrons that strike inside this particular value of δ fail to emerge, or would if the theory represented all of the facts. They are of the class of electrons that, as shown by Darwin, spiral into the nucleus.

On the simple theory

$$\delta^2 = \frac{1 - \cos \Psi}{[(2\mu - 1)^2 + 1] + [(2\mu - 1)^2 - 1] \cos \Psi}.$$

The family of curves corresponding to this equation is shown in Fig. 5. The analogues of the various properties of the distribution curves shown in Fig. 2 may be easily recognized.

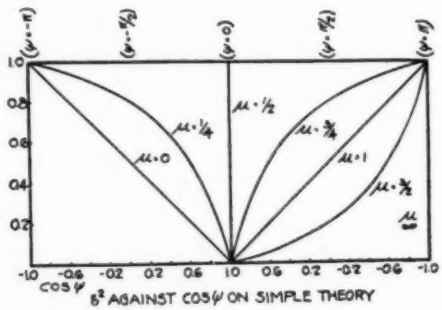


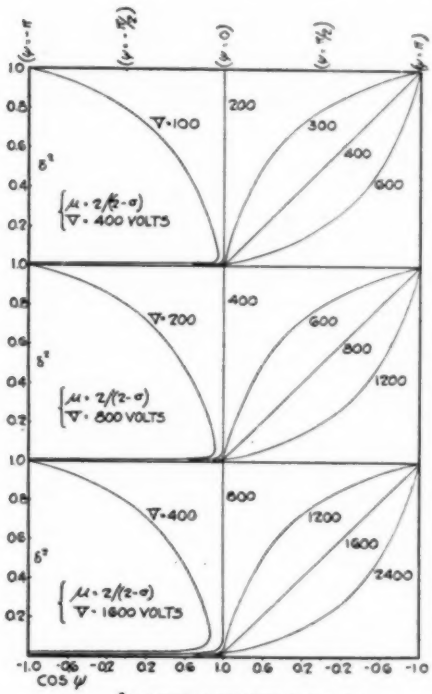
Fig. 5

Three corresponding families of curves based on the more complete theory are shown in Fig. 6. The curves in the first of these are for the case in which $\mu = 2/(2 - \sigma)$ corresponds to $V = 400$ volts. For a fixed system (ρ and E constant) μ is proportional to V, so that $\mu = 1/(2 - \sigma)$ corresponds very closely to $V = 200$ volts, etc. The second and third families are for the cases in which $\mu = 2/(2 - \sigma)$ corresponds respectively to $V = 800$ volts and $V = 1{,}600$ volts.

It is evident from these curves that the variation in mass of the electron with velocity will cause departures from the distributions shown in Fig. 2 that are more marked the greater the value of E/ρ for the scattering system. Zero voltage curves do not appear in these families. As the voltage decreases the number of electrons which on the theory spiral into the nucleus increases and finally includes all at a bombarding potential $V = (e/2mc^2) \cdot (E^2/\rho^2)$ e.s.u. E/ρ is the potential for which $\mu = 1$. If we represent this by $\overline{V}$ and express potentials in volts, the limiting voltage is given by $V = 9.8 \times 10^{-7}\ \overline{V}^2$.

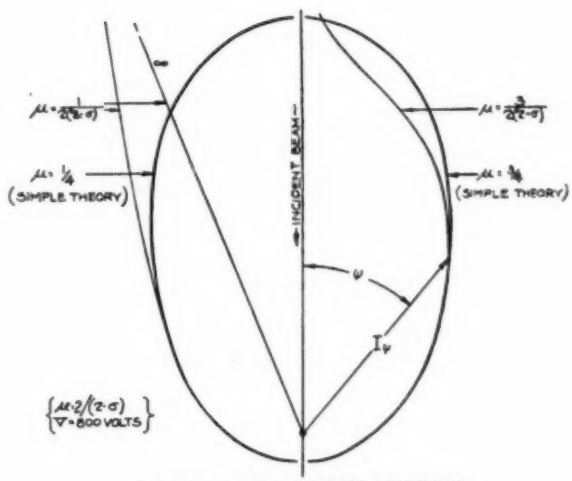
For the curves shown in Fig. 6 these limiting voltages are 0.16, 0.63 and 2.5 volts respectively.

Distribution curves constructed from the δ^2 against cos Ψ curves are shown in Fig. 7 together with the corresponding distribution curves of



δ² AGAINST COS ψ ON BASIS OF DARWIN'S ORBITS

Fig. 6



COMPARISON OF DISTRIBUTION PATTERNS
(CONIC ORBITS AND DARWIN ORBITS)

Fig. 7

the simple theory. These are for the case $\mu = 2/(2 - \sigma)$ corresponding to $V = 800$ volts.

It is evident that for $\mu < \frac{1}{2}$ the effect of the variation in mass of the electrons with speed is to increase the intensity of scattering in directions for which $\Psi < \pi/2$, except for a range of Ψ near zero where the intensity should be negligible. For $\mu > \frac{1}{2}$ the intensities in the directions $\Psi < \pi/2$ are less, except near $\Psi = 0$, than on the simple theory, but these departures are less important.

To a certain extent the results of this calculation can be made to account for the discrepancies between the observed scattering patterns for magnesium and the requirements of the simple theory. On the other hand, the special feature of the latter calculation—the very great intensity of scattering at a critical angle for the lowest voltages—appears to be altogether lacking. As already stated, we hope to publish the experimental results very soon.

In a recent article on the scattering of β-rays H. A. Wilson [1] has taken a view in regard to the motion of an electron in the field of a positive nucleus which differs in an important respect from that held by Darwin. In his calculation Darwin assumed that an electron moving in the field of a positive nucleus has the same mass characteristics as that of an electron of equal speed isolated in space. The longitudinal and transverse masses were set down as $m(1 - v^2/c^2)^{-3/2}$ and $m(1 - v^2/c^2)^{-1/2}$ respectively, and the trajectory was calculated for a particle having these mass characteristics when acted upon by a central inverse square force. This led to the pseudo-conic orbits considered in the preceding section. It is fairly clear that this procedure is correct only in the case in which the forces acting on the electron are non-electrical in nature, that is, in the case in which the electron preserves its individual field. In the actual case the time changes which give rise to kinetic energy and momentum occur, not in the field of an isolated electron, but in the mutual field of electron and nucleus. A rigorous treatment of the problem would evidently have to be based on the momentum and energy integrals of this mutual field. Wilson, in his treatment of the problem, has assumed that such a calculation will simply lead to the conclusion that the kinetic energy and angular momentum associated with the electron are proportional, not to the electrostatic energy of the isolated electron, but to this energy plus one half of the mutual energy of the two charges. In other words, it is assumed that the system will behave as if one half of the mutual energy moves with the electron, the other half remaining at rest with the nucleus.

[1] H. A. Wilson, Proc. Roy. Soc. A **102**, p. 9 (Oct. 2, 1922).

The very important difference that this assumption makes is that all orbits turn out to be conic. This results, apparently, from a compensation of the increase in mass of the electron regarded as an isolated charge, by a decrease in mass by what, in another connection, is referred to as "packing." The only difference between the orbit of the electron and that of a particle of constant mass moving in an inverse square field is, according to Wilson's solution of the problem, that the mass of the electron, though constant in a given orbit, varies from one orbit to another. The variations are unimportant, however, in all cases in which the speed of the electron at an infinite distance from the nucleus is small compared with the velocity of light. It follows, therefore, that if Wilson's assumption in regard to the rôle played by the mutual energy is correct, the scattering patterns for low speed electrons should be sensibly the same as those calculated on simple theory.

Wilson's paper includes a calculation of the deflection of an electron in a limited field which is similar to that derived on the simple theory, and also a calculation of the sum of the squares of such deflections for the system under random bombardment by high speed electrons approaching on parallel lines. It does not, however, include a calculation of the angular distribution of scattered particles.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY,
AND THE WESTERN ELECTRIC COMPANY, INCORPORATED,
December 16, 1922

THE DEFLECTION OF A STREAM OF ELECTRONS BY ELECTROMAGNETIC RADIATION.

By E. O. Hulburt.

Abstract.

Deflection of a stream of electrons by electromagnetic radiation.—*A theoretical calculation*, based on classical electrodynamics, gives for the maximum angular deflection, when certain approximations are made, $He/m\omega$, where $\omega/2\pi$ is the frequency of the radiation, and H is the field due to it. For sunlight ($H = .04$) the value is only 4×10^{-10}, far too small to detect experimentally, while for intense x-rays, the value is of the order of 10^{-13}. Recently C. J. Lapp reported having obtained an observable deflection with x-rays. If further research should confirm this result, it would appear to be in direct conflict with the classical theory.

SOME time ago the writer determined from the classical equations of electrodynamics the path of an electron which moved in an alternating electromagnetic field. Renewed interest arose in the problem as the result of an experiment performed by C. J. Lapp[1] on "the effect of short electromagnetic waves on a beam of electrons," in which a strong beam of x-rays appeared to produce a deflection of a stream of electrons traversing the beam. The outcome of the theoretical calculation indicated, however, that no observable deflection would be expected unless a very sensitive method of detection were used. The details of the calculation follow.

A rigid electron of mass m and charge e moves initially along X with a velocity v in the midst of a plane polarized electromagnetic wave of frequency $\omega/2\pi$. The wave is propagated in the direction of X and the magnetic and electric vectors are $H_z = H \cos \omega t$ and $E_y = E \sin \omega t$, respectively, where H and E are the amplitudes. The reaction on the motion due to radiation from the electron is neglected. If x, y, and z are the positional coördinates of the electron at time t and electromagnetic units are used, the equations of motion of the electron are, in Newtonian notation,

$$\begin{aligned} \frac{m}{e}\ddot{x} &= -H\dot{y}\cos\omega t, \\ \frac{m}{e}\ddot{y} &= H\dot{x}\cos\omega t + E\sin\omega t, \\ \frac{m}{e}\ddot{z} &= 0. \end{aligned} \tag{1}$$

[1] Physical Review, 20, 104, 1922.

Suppose initially $t = x = y = z = \dot{y} = \dot{z} = 0$ and $\dot{x} = v$. We see from (1) that z always remains zero and therefore we may concern ourselves only with the motion in the XY plane. The direct elimination of t from (1) leads to a differential equation in x and y which is difficult to integrate. We thereupon content ourselves with an approximate solution. Letting $\theta = \omega t$, (1) becomes

$$\begin{aligned} \frac{d^2x}{d\theta^2} &= -\frac{He}{m\omega}\frac{dy}{d\theta}\cos\theta, \\ \frac{d^2y}{d\theta^2} &= \frac{He}{m\omega}\frac{dx}{d\theta}\cos\theta + \frac{Ee}{m\omega^2}\sin\theta. \end{aligned} \tag{2}$$

It is assumed that ω is such a large quantity that the last term of the second equation of (2) may be neglected. This term is of the nature of a perturbing term and our assumption amounts to the omission of a small perturbation from the motion. Equations (2) then become, approximately,

$$\begin{aligned} \frac{d^2x}{d\theta^2} &= -\frac{He}{m\omega}\frac{dy}{d\theta}\cos\theta; \\ \frac{d^2y}{d\theta^2} &= \frac{He}{m\omega}\frac{dx}{d\theta}\cos\theta. \end{aligned} \tag{3}$$

Multiplying the first equation of (3) by $dx/d\theta$ and the second by $dy/d\theta$ and then adding leads to

$$\frac{d}{d\theta}\left[\left(\frac{dx}{d\theta}\right)^2 + \left(\frac{dy}{d\theta}\right)^2\right] = 0.$$

From this it follows that the speed of the electron in its path is constant.

When equations (3) are solved by expanding x and y as power series and by introducing the initial conditions, it is found that

$$x = \frac{v}{\omega}\theta; \qquad y = \frac{Hev}{m\omega^2}(1 - \cos\theta). \tag{4}$$

This is an approximate solution, obtained by neglecting terms in $He/m\omega^n$, where n is greater than 2. Remembering that $\theta = \omega t$, equations (4) become

$$x = vt, \qquad y = \frac{Hev}{m\omega^2}(1 - \cos\omega t), \tag{5}$$

which show that the electron pursues a sine curve in the XY plane, of small amplitude $He/2m\omega^2$ and of frequency $\omega/2\pi$. The direction in which the electron is moving is given by $dy/dx = He/m\omega \sin \omega t$, and

when $\omega t = \pi/2$, this has the maximum value

$$\left[\frac{dy}{dx}\right]_{\max} = \frac{He}{m\omega}. \tag{5}$$

We proceed to estimate the energy density of the x-radiation from a Coolidge tube. The energy of the cathode rays in a Coolidge tube under normal operation is about 200 watts. According to R. T. Beatty[1] perhaps the fraction 5×10^{-4} of the cathode ray energy goes into the general x-ray spectrum. If the characteristic radiation of the target is excited, a larger fraction of the energy passes into the emitted x-rays. The x-ray beam from the Coolidge tube of course diverges, but let us assume that all the x-ray energy is confined to a beam of a uniform cross section of 1 cm^2. The energy density of the x-radiation is then 3×10^{-5} ergs/cm^3.

Poynting's theorem states that the energy density of a plane sine wave is $\mu H^2/8\pi$, where H is the amplitude of the magnetic vector. If the conditions of Poynting's expression apply to the foregoing x-radiation we find, when the magnetic permeability μ is placed equal to unity, that $H = 0.03$ gauss. If the x-radiation is assumed to have a wave-length 10 A. U., ω is of the order of 10^{18}. Introducing these values into (5) and taking e/m to be 1.7×10^7 we find $[dy/dx]_{\max}$ to be of the order of 10^{-13}. This is a small quantity, so small in fact that although our estimates may be considerably in error and although the conditions of Lapp's experiment were more complex than those imagined in our calculation, we feel justified in concluding that the observed deflection of the electron beam seems to be at variance with the result to be anticipated from the classical equations.

It may be noted that even in the case of sunlight, since the maximum value of H is 0.04 gauss and ω is 1.6×10^{15}, $[dy/dx]_{\max}$ is only about 4×10^{-10}.

UNIVERSITY OF IOWA,
November 23, 1922.

[1] Royal Society Proceedings, *A*, 89, 314, 1913.

ON THE THEORY OF THE TEMPERATURE VARIATION OF THE SPECIFIC HEAT OF HYDROGEN

By E. C. Kemble and J. H. Van Vleck

Abstract

Quantum theory of rotational and vibrational specific heats of an elastic, non-gyroscopic model of a diatomic gas.—To account for the abnormally large specific heat of hydrogen at high temperatures, the molecule is assumed to have an internal vibrational degree of freedom. Assuming a dumb-bell model and the following law of force $F = a(r - r_0)/r^3$, the energies of the stationary states are derived on the basis of the Bohr-Sommerfeld form of the quantum hypothesis, and an expression for the specific heat obtained. When suitable values of the two adjustable constants are chosen, satisfactory agreement is obtained with the experimental results for hydrogen throughout the entire range, to 1300° K.

Constants of the hydrogen molecule, computed from the empirical constants of the specific heat equation are: Nuclear spacing, 0.488×10^{-8} cm; moment of inertia, 1.975×10^{-41} gm cm^2; wave-length corresponding to normal vibration, 2.05 μ.

Specific heats of hydrogen and water vapor; new empirical formulas for temperatures between 300° and 2300° K derived from Pier's data, are given: For hydrogen: $c_v = 4.87 + 0.539 \times 10^{-3}t + 0.146 \times 10^{-6}t^2$; for water vapor: $c_v = 6.03 + 4.2 \times 10^{-3}t - 4.07 \times 10^{-6}t^2 + 1.95 \times 10^{-9}t^3$.

Introduction

THE problem of explaining the abnormal specific heat of hydrogen at low temperatures has engaged the attention of numerous investigators.[1] The theory most generally accepted at the present time was first formulated by one of the writers of this paper in an unpublished doctor's dissertation in 1917.[2] A brief account of the theory was given in a paper read before the American Physical Society in October, 1917.[3] This paper was unfortunately marred by an error made in an attempt to take into account the expansion of the molecule due to centrifugal force at the larger rotational speeds. The publication of the details of the theory was delayed by the war and in 1919 Reiche,[4] working independently, published a complete discussion of the problem based on a rigid model of the molecule and differing only in minor respects from that contained in the above-mentioned thesis.

[1] For a resumé of the results see F. Reiche, "Die Quantentheorie," Berlin, 1921.

[2] E. C. Kemble, "Studies in the Application of the Quantum Hypothesis to the Kinetic Theory of Gases and to the Theory of their Infra-red Absorption Bands," Harvard University, 1917.

[3] E. C. Kemble, Phys. Rev. **11**, p. 156, 1918 (abstract).

[4] F. Reiche, Ann. der Phys. **58**, p. 657, 1919.

The purpose of the present paper is to present a corrected calculation of the rotational and vibrational specific heat of an elastic model of a diatomic gas molecule. Such a calculation is desirable since the observed specific heat of hydrogen at high temperatures is appreciably greater than the limiting theoretical value for rigid molecules, $(5/2)R$ or 4.963 calories per mol. We cannot correct for the effect of elasticity simply by adding to the specific heat of a rigid molecule the vibrational specific heat of an ideal linear oscillator, for the expansion of the molecule by centrifugal force must be taken into account.[1] This expansion alters the energies of the stationary states corresponding to various values of the angular momentum and thus causes an increase in the rotational specific heat. The effect is largest for those molecules with the smallest moments of inertia and hence is particularly important for hydrogen.

In this connection it may be observed that the classical statistical mechanics does not demand a constant rotational specific heat as is commonly assumed. The equipartition law specifies the average kinetic energy of rotation for a diatomic gas to be RT. If the molecules are regarded as elastic a rotational potential energy must be added which is roughly proportional to the square of the kinetic energy. It follows that the complete rotational specific heat is an approximately linear function of T having the value R as a lower limit. Needless to say, the correction is small for most molecules at moderate temperatures.

Determination of the Energies of the Stationary States

The first part of the problem of computing the specific heat for a model of a gas molecule consists in the application of the quantum conditions to the determination of the energies of the stationary states. In order to get a definite result we must introduce an assumption regarding the nature of the law of force binding the nuclei of the two atoms together. A good deal of information regarding the nature of the law for the HCl molecule can be obtained from the study of its infra-red band spectrum, but we have no sure hold, either experimental or theoretical, on the law for the hydrogen molecule. We know, however, that when the nuclei are close to their equilibrium positions the restoring force must be an approximately linear function of the displacement. For large displacements, on the other hand, the force must drop off as the inverse square of the distance between the nuclei, or more rapidly. These two requirements are conveniently met by the assumption that the force is of the form

$$F = a(r - r_0)/r^3. \tag{1}$$

[1] This expansion is the cause of the asymmetry of the infra-red absorption bands of polar diatomic gases.

Here r is the distance between the nuclei, r_0 the equilibrium value of r, and a is a constant, which may be adjusted to give the frequency of vibration any desired value. The equations of motion resulting from the law stated above are mathematically of the same general form as those which govern the motion of an electron around a single hydrogen nucleus when the relativity correction is taken into account. Consequently by postulating a force of the form given in (1) we can carry through the determination of the energies of the permitted motions without further approximations. Of course this law is not to be considered as actually correct, but fortunately auxiliary computations indicate that an accurate formula for large displacements is not needed over the range of temperatures considered in this article.

Let the angular and radial momenta be denoted by p_φ and p_r respectively. Denoting the masses of the nuclei by m_1 and m_2 and introducing the abbreviation $\mu = m_1m_2/(m_1 + m_2)$, we readily derive the following expression for the energy (Hamiltonian function):

$$W = \frac{p_\varphi^2}{2\mu r^2} + \frac{p_r^2}{2\mu} + \frac{a}{2r_0} - \frac{a}{r} + \frac{ar_0}{2r^2}. \tag{2}$$

The application of the Wilson-Sommerfeld quantum conditions yields the relations [1]

$$p_\varphi = mh/2\pi, \qquad m = 0, 1, 2, 3, \cdots, \tag{3}$$

and

$$\oint p_r dr = -2\pi\left[\sqrt{p_\varphi^2 + \mu a r_0} - \frac{\mu a}{\sqrt{2\mu(a/2r_0 - W)}}\right] = nh, \qquad n = 0, 1, 2, 3, \cdots. \tag{4}$$

Solving the above equations for the total energy W as a function of the quantum numbers m and n, we obtain

$$W = \frac{a}{2r_0}\left[1 - \frac{4\pi^2\mu a r_0}{h^2(n + \sqrt{m^2 + 4\pi^2\mu a r_0/h^2})^2}\right]. \tag{5}$$

We denote by ν_0 the frequency of vibration of a non-rotating molecule with an infinitesimal amplitude. This may be proved to be

$$\nu_0 = (1/2\pi)\sqrt{a/\mu r_0^3}. \tag{6}$$

From the definition of the angular momentum p_φ the following expression for the angular velocity is readily deduced:

$$\omega = p_\varphi/\mu r^2 = mh/2\pi\mu r^2.$$

[1] In the earlier work by Kemble the condition (3) was derived from Planck's cell theory by introducing the assumption that the permitted stationary states are those whose representative points lie on the cell boundaries. Cf. M. Planck, Verh. d. D. Phys. Ges. **17**, p. 407, 1915.

Hence, to a close approximation, the frequency of rotation of a non-vibrating molecule with a single unit of angular momentum is

$$\nu_1 = h/4\pi^2\mu r_0^2. \tag{7}$$

The frequency of rotation for a rigid molecule would be an integral multiple of ν_1. With the aid of Eqs. (6) and (7) the expression for the energy can be thrown into the form

$$W_m{}^n = \frac{h\nu_1}{2}\left(\frac{\nu_0}{\nu_1}\right)^2\left[1 - \frac{1}{\{(\nu_1/\nu_0)n + \sqrt{1 + (\nu_1/\nu_0)^2 m^2}\}^2}\right]. \tag{8}$$

In most applications of this theory the ratio ν_1/ν_0 will be a small number. The value derived from the infra-red band spectrum of HCl is 0.0076. In applying the above expression to hydrogen we may treat ν_1 and ν_0 as adjustable constants whose values may be chosen to fit the experimental specific heats. From the values of these constants used in obtaining the curves given later in this article and from the assumed law of force we may compute the energy required to break up the molecule.[1] This has the right order of magnitude, being about 40 per cent greater than the heat of dissociation as observed by Langmuir. No better agreement could be expected in view of the fact that our law of force makes no pretence at accuracy for large values of r.

Calculation of Specific Heat

Let N denote the number of molecules in a gram molecule and let $p_m{}^n$ denote the intrinsic probability of the stationary state mn. The rotational and vibrational energy E of a gram molecule of gas at the temperature T may be computed from Planck's formula [2]

$$E = N\frac{\sum_n\sum_m p_m{}^n W_m{}^n e^{-W_m{}^n/kT}}{\sum_n\sum_m p_m{}^n e^{-W_m{}^n/kT}}, \tag{9}$$

in which the average energy of the molecules in the "region element" mn (Planck's second theory) is replaced by the energy $W_m{}^n$ of the molecules in the stationary state associated with this region element.[3]

The corresponding expression for the specific heat is obtained by differentiation with respect to T. It is

$$c = \frac{Nk}{J}\left[\frac{P_3}{P_1} - \left(\frac{P_2}{P_1}\right)^2\right] \tag{10}$$

[1] The formula for energy of dissociation is $(h\nu_1/2)(\nu_0/\nu_1)^2$.

[2] Planck, Verh. d. D. Phys. Ges. **17**, p. 412, 1915.

[3] Each of the quantum conditions defines a family of surfaces in the state-space of statistical mechanics. These surfaces divide this space into cells which may be identified with Planck's region elements.

where J = mechanical equivalent of heat; $P_1 = \sum_n \sum_m p_m^n e^{-\sigma_m^n}$; $P_2 = \sum_n \sum_m p_m^n \sigma_m^n e^{-\sigma_m^n}$; $P_3 = \sum_n \sum_m p_m^n (\sigma_m^n)^2 e^{-\sigma_m^n}$; $\sigma_m^n = W_m^n/kT$. In evaluating the above series, the stationary state ($m = 0$, $n = 0$) is assumed to have zero probability as indicated by the infra-red absorption bands of diatomic gases.[2] At the highest temperatures used the series need to be summed to 13 terms in m, and 3 terms in n. It is of interest to note that strictly speaking they are only semi-convergent since W_m^n and the exponential factor approach finite limits as m and n become infinite.

It remains to discuss the formula to be used for the intrinsic probability p_m^n. Planck assumes that the probability of each cell is proportional to the volume of that cell as in the classical statistical mechanics, and we follow the line of least resistance in identifying the cell probability of his theory with the probability of the corresponding stationary state in the new theory. Since, however, the stationary state of zero energy ($m = 0$, $n = 0$) is arbitrarily ruled out, there is more than one way of assigning the remaining states to the cells, and consequently this point of view leads to an ambiguous set of values for the p's.

Reiche makes use of the fact that an external electric or magnetic field will break up each of the stationary states into new ones having (on the basis of Planck's hypothesis) unit intrinsic probability. He therefore identifies p_m^n with the number of new states between which the molecules having m units of angular momentum are divided by the field.[1] The application of the quantum conditions to the angular coördinates in the presence of a magnetic field involves the use of two quantum numbers. One, which we denote by the symbol m_1, gives the number of units of angular momentum parallel to the field. If the stationary states corresponding to all values of both numbers are recognized as equally probable, the value of p_m^n is easily shown to be $2m + 1$. On the other hand, if we rule out those states for which m_1 is zero, following an argument due to Bohr, p_m^n works out to be $2m$. Specific heat calculations based on a rigid model of the hydrogen molecule favor the latter formula for p_m^n.

Comparison of Theoretical and Experimental Values

Hydrogen.—The form of the specific heat curve for hydrogen between 35° K and 350° K has been pretty well established by the experiments of

[1] Since Reiche deals with rigid molecules the quantum number n does not appear n his analysis.

Eucken,[1] Scheel and Heuse,[2] and Escher.[3] Less trustworthy determinations of the specific heat at higher temperatures have been made by Crofts [4] from observations of the ignition temperatures of adiabatically compressed mixtures of electrolytic gas and hydrogen, and by Pier [5] and others using the explosion method.

While the observations of Pier are the latest and apparently the best for very high temperatures, his formula does not agree at low temperatures with the well-established results of other investigators. We therefore attempted at first to fit our formula at high temperatures to a point taken from the work of Crofts.[6] The result of these initial calculations was unsatisfactory. Whether the intrinsic probability $p_m{}^n$ is set equal to $2m$ (curve B' in the accompanying graph) or to $2m + 1$ (curve B), it is impossible to pass a curve through the Crofts point which will also fit the observations near 300° K.

We have accordingly made a study of Pier's data which shows that the discrepancy between his formula (see Eq. (14) below) and the well-established points in the neighborhood of 300° K is not inherent in his observations. By combining the value of the specific heat at 289° K given by Scheel and Heuse with Pier's data we have derived a new empirical formula which fits the latter set of points better than the original one. Pier determined the average specific heats at constant volume of various mixtures of water vapor, argon, and hydrogen between 17° C and temperatures ranging from 1400° C to 2350° C. We have assumed the specific heat of argon to be 2.98 calories per mol and have set the specific heats of water vapor and hydrogen at 17° C equal to 6.1 [7] and 4.88 (Scheel and Heuse) respectively. The following formulas were then deduced by a semigraphical method which need not be described in detail: For water vapor, $0 < t < 2300°$ C,

$$C_v = 6.03 + 4.2 \times 10^{-3}t - 4.07 \times 10^{-6}t^2 + 1.95 \times 10^{-9}t^3, \quad (11)$$

For hydrogen, $0 < t < 2300°$ C,

$$C_v = 4.87 + 0.539 \times 10^{-3}t + 0.146 \times 10^{-6}t^2, \quad (12)$$

[1] A. Eucken, Sitz. d. Kon. Preus. Akad. d. Wis. 1, p. 141, 1912.

[2] K. Scheel u. W. Heuse, Ann. der Phys. (4) 40, p. 473, 1913.

[3] W. Escher, Ann. der Phys. (4) 42, p. 761, 1913.

[4] J. M. Crofts, J. Chem. Soc. 107, p. 290, 1915.

[5] M. Pier, Zeits. f. Elektrochemie, 15, p. 356, 1909.

[6] Crofts gives 5.10 calories per mol as the mean specific heat between 15° C and 532° C. We have assumed that this value can be used for the specific heat at the average temperature 273° C, or 546° K.

[7] Cf. H. Levy, Verh. d. D. Phys. Ges. 11, p. 331, 1909. All specific heats are for the ideal gas condition.

Pier's own formulas are,[1] for water vapor

$$C_v = 6.065 + 1.0 \times 10^{-3} t + 0.8 \times 10^{-6} t^3 \qquad (13)$$

and for hydrogen

$$C_v = 4.70 + 0.9 \times 10^{-3} t. \qquad (14)$$

There is apparently a misprint in Pier's published record of his 134th experiment, for we cannot check his calculation for that point. Discarding this one observation, we find that the sum of the squares of the residual errors is reduced 48 per cent by the changes we have introduced in the formulas.

Curve *a*, Fig. 1, is plotted from Pier's formula (14). Curve *b* is a plot

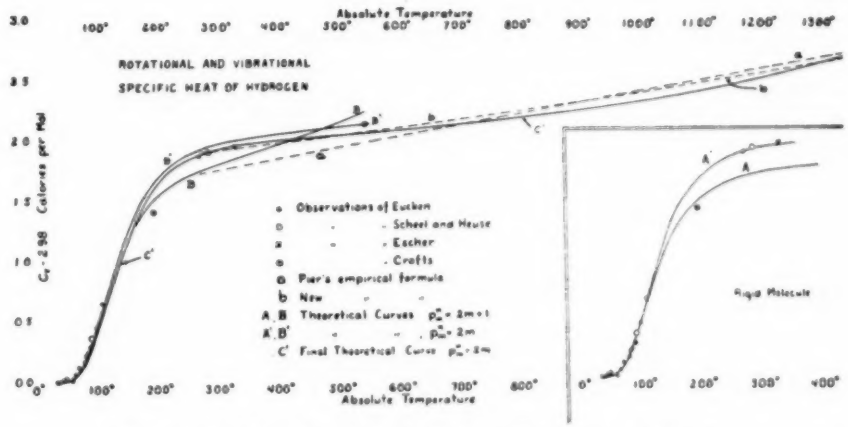


Fig. 1. Rotational and vibrational specific heat of hydrogen.

of (12), which we believe to be the best available empirical estimate of the high temperature specific heat of hydrogen. Taking the point at 1350° K on this curve as standard for fixing an approximate value of ν_0, we have plotted the theoretical curve C' from our formulas (8) and (10), giving $p_m{}^n$ the value $2m$. It will be seen that the agreement between this last curve and the measured specific heats is quite satisfactory. A calculation for 2006° K, which does not appear on the graph, shows a discrepancy of 0.27 cal/mol, between the theoretical curve C' and the empirical curve *b*. In view of the fact that an error in the assumed form of the law of force would begin to make itself felt at such a high temperature as this, and considering the experimental uncertainty involved, the discrepancy is small. We thus obtain a simultaneous confirmation of our theory and of the Pier measurements of the specific

[1] Pier gives the formulas for the mean specific heats only. Eqs. (13) and (14) are the corresponding expressions for the instantaneous specific heats.

heat at high temperatures.[1] The formula for p_m^n used in calculating the theoretical specific heats confirms the conclusion of Reiche but conflicts with the result previously obtained by Kemble.

Table I. gives the numerical values from which the graph was plotted.

TABLE I.

Rotational and vibrational specific heat of hydrogen

Absolute temp.	A	A'	B	B'	C'	Observed	Source
60°					.020	.01	(1)
65	.060	.052	.059			.06	(1)
80	.183	.167	.182		.133	.16	(1)
100	.441	.441	.441	.44	.404	.44	(1)
110	.590	.599	.588		.521	.64	(1)
145		1.147			1.058		
149	1.098		1.109				
196.5	1.449	1.622	1.488		1.584	1.41	(1)
196.5						1.401	(2)
273		1.858	1.741	1.91	1.872	1.86	(1)
289			1.77	1.94	1.898	1.897	(2)
333	1.72	1.92	1.84	1.99	1.948	1.935	(3)
450			2.03	2.07			
546			2.22	2.12		2.124?	(4)
625					2.07	2.10	(5)
1000					2.28	2.36	(5)
1349					2.66	2.64	(5)
2005.6					3.532	3.263	(5)

Sources: (1) Eucken; (2) Scheel and Heuse; (3) Escher, mean value 293°–373°; (4) Crofts, mean value 288°–805°; (5) Empirical equation (12) from Pier's data.

From the values of the constants used in adjusting the curve C' we deduce the following *magnitudes for the hydrogen molecule:*

λ_0 = wave-length corresponding to the normal vibration frequency of the H_2 molecule = 2.05 μ;

L_0 = normal moment of inertia of H_2 molecule = 1.975×10^{-41} gm cm^2;

r_0 = normal nuclear spacing = 0.488×10^{-8} cm.

Reiche's value for L_0 is 2.095×10^{-41} gm cm^2.

It is worthy of note that up to 1350°, at least, the rotational specific heat exceeds the limiting value for a rigid molecule (1.985 cal/mol) by more than the corresponding vibrational specific heat. This shows the impossibility of calculating high temperature specific heats of gases by

[1] Pier's work has been criticized by Bjerrum because of his failure to take into account the heat lost to the walls of the calorimeter before the pressure maximum, but the hypothesis that this loss is small is supported by Siegel in a later paper. The experiments of Womersley also seem to indicate that the heat loss to the walls is small, though his report is so brief that it is obscure. Cf. N. Bjerrum, Zeits. f. Elektrochem. **17**, 731 (1911); W. Siegel, Zeits. f. Phys. Chemie, **87**, 641 (1914); W. D. Womersley, Proc. Rov. Soc. A. 100, p. 483 (1922).

simply adding the specific heat of one or more ideal linear oscillators of suitable frequencies to the classical specific heat for a rigid molecule of the type in question.

Other diatomic gases.—While we have much less complete data on other diatomic gases than hydrogen, abnormally low specific heats have been calculated by Scheel and Heuse from their observations on nitrogen, oxygen, and carbon monoxide in the neighborhood of 92° K. Assuming that the Reiche formula for the specific heat of a rigid molecule ($p_m = 2m$) can be applied to these gases we may calculate the moments of inertia and nuclear separation from the observations in question. Table II.

TABLE II.

Gas	t	c_{v_0} calculated by Scheel and Heuse cal/mol	Rotational sp. heat cal/mol	Moment of inertia J 10^{-41} gm cm^2	Nuclear spacing 10^{-9} cm
N_2.....	−181° C	4.733	1.755	5.16	2.1
O_2.....	−181	4.91	1.93	8.11	2.47
CO.....	−180	4.758	1.780	5.3	2.16

shows the result of such a calculation. The values of the distance between the atomic nuclei are absurdly small in comparison with the nuclear spacing for H_2 or with estimates of the radii of the atoms of oxygen, nitrogen, and carbon made in other ways. They force the conclusion that either the assumed specific heats are wrong, or that the theory is not applicable to these gases.

It hardly seems probable that there can have been any considerable error in the observations of Scheel and Heuse, which were made on c_p at atmospheric pressure. The calculation of the specific heat at constant volume in the ideal gas condition involves a considerable correction for pressure, however, which may be inaccurate.

As regards the applicability of the theory to these gases it should be observed that we have assumed our molecular model to be non-gyroscopic. The positive magnetic susceptibilities of O_2 and N_2 suggest that these gases do not fall in the non-gyroscopic class and it is possible that carbon monoxide does not lie within the scope of the present theory for the same reason.

Our thanks are due to Mr. K. C. Mazumder for his assistance in working up Pier's data.

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December 13, 1922

THE COEFFICIENT OF VISCOSITY OF HELIUM AND THE COEFFICIENTS OF SLIP OF HELIUM AND OXYGEN BY THE CONSTANT DEFLECTION METHOD

By M. N. States

Abstract

Coefficient of viscosity of helium by the constant deflection method.—Using carefully purified He, which showed only a spectroscopic trace of H, six series of measurements at about 23° C gave $\eta_{23} = 1962.3\ (10)^{-7}$. This is about 2 per cent less than values obtained by the capillary method, but is believed correct to within 0.1 per cent.

Coefficients of slip of helium and oxygen for polished and unpolished silver oxide surfaces.—The values obtained for $\zeta_{76}\cdot(10)^7$ are: for the unpolished surface, 123 (He), 61.1 (O); for the polished surface, 160 (He), 64.5 (O). These are probably accurate to one per cent. From Maxwell's equation, the values for complete diffuse reflection, which are the minimum values, are computed to be 191 (He) and 70 (O). The low experimental values suggest a "reverse-specular" reflection or perhaps the abnormal momentum transfer at the surface may be attributed to an excess of molecules leaving the cylinders due to the release of oxygen at low pressures. The change of the slip with time, observed in previous work, is shown to be due to the release of occluded gases, chiefly oxygen in the case of a silver oxide surface.

Increase in the stiffness of the steel suspension wire, noted by Van Dyke, continues.

Introduction

THE recent work of Stacy [1] and Van Dyke [2] on the coefficients of slip of air and carbon dioxide showed clearly that these quantities depend upon the nature of the bounding surfaces. The coefficient of slip was larger for the smoother surfaces, indicating that these reflected a greater number of molecules specularly. For old shellac (the "roughest surface" used), however, both of these observers found a nearly diffuse reflection for air; *i.e.*, the molecules were reflected or re-emitted from the surface at no favored angle. This conclusion is based on Maxwell's [3] expression for the value of the coefficient of slip

$$\zeta = \frac{1}{2}\eta\sqrt{\frac{2\pi}{p\rho}}\cdot\left(\frac{2}{f}-1\right) \qquad (1)$$

when a fraction f of the molecules is diffusely reflected and a fraction $(1-f)$ is considered specularly reflected from the surface; their result

[1] Stacy, Phys. Rev. 21, 239 (1923).
[2] Van Dyke, Phys. Rev. 21, 250 (1923).
[3] Maxwell, Scientific Papers 2, 708.

came out nearly equal to the value calculated for $f = 1$. This value corresponding to $f = 1$ should be the minimum possible value of the slip.

It was thought desirable to make a study of the coefficient of slip, using different surfaces and other gases, in order to test this minimum value further. In addition, the chemical composition of the surface used afforded an excellent opportunity for studying the "time effect" on the slip. Finally, the coefficient of viscosity of helium was determined.

The Apparatus[1]

The constant deflection method was used, the apparatus being that with which Gilchrist[2] and Harrington[3] determined the absolute value of the coefficient of viscosity of air. Such a complete description of the apparatus used in the above work has been given that it will be sufficient here to indicate only what changes have been made since the apparatus was used by Van Dyke.

A sliding pulley which fed the cord to the drum of the driving mechanism was eliminated and two ball bearing pulleys made from bicycle hubs were substituted for the two ordinary pulleys which carried the driving weights. These changes in the driving mechanism made a decided improvement in the constancy of the speed of rotation of the outer cylinder, as evidenced by the chronograph record, and a corresponding improvement in the steadiness of the deflection of the inner cylinder. Static charges, it was observed, produced a deflection of the inner cylinder, the steel suspension wire being attached to a glass tube which insulated the inner cylinder from the ground. Accordingly, as an added precaution, the entire inner system was grounded, although observations were not taken when such disturbing effects were present.

The brass cylinders were coated with a layer of silver oxide of the order of 0.001 mm in thickness which constituted the "first" surface. This layer was formed by the displacement of the metal in the brass by the silver in a solution of silver nitrate, the silver immediately oxidizing. The cylinders were rotated in the solution during this process so that a uniform coat was obtained. The deposit was allowed to dry thoroughly in air before the cylinders were set in place, and then stood about five months, for the most part at low pressure, before the first observations

[1] It is interesting to note that A. Timiriazeff used an apparatus somewhat similar to the above for coefficient of slip and viscosity determinations. For slip determinations he used pressures of the order of .001 mm of mercury and calculated his results in a slightly different manner. His values for the coefficients of viscosity for air, carbon dioxide, and hydrogen are from eight to fifteen per cent higher than those obtained by other observers. Ann. der Phys. **40**, 971 (1913).

[2] Gilchrist, Phys. Rev. **1**, 124 (1913).

[3] Harrington, Phys. Rev. **8**, 738 (1916).

here recorded were taken. A second set of observations was taken for the coefficient of slip after the oxide had been burnished with paper and polished with chamois.

The evacuating system consisted of a mercury diffusion pump supported by a May-Nelson pump. The latter was thoroughly over hauled, the tubes leading from the pumps being enlarged so that the time of evacuation was considerably reduced. In the case of helium a complete set of data for the determination of the value of the coefficient of slip could be obtained within twenty minutes after the gas was introduced into the apparatus. Stacy, using a Gaede pump, was able to take similar observations only after two hours of pumping. Van Dyke, however, in the latter part of his work reduced this time to one hour for slip determinations at a pressure of about 0.1 mm of mercury. After it was found that the slip determinations here recorded plotted against time gave a straight line parallel to the time axis, no special effort was made to hurry the evacuation.

The constant temperature room was kept close to 23° C by means of an electric heater controlled by an ether thermostat. The temperature within the apparatus was read on a Beckmann thermometer which was compared with a standard Baudin thermometer before and after this series of data was taken. The Beckmann showed no change in calibration in this period of five months. With a fan constantly circulating the air in the room, the variation of the temperature within the apparatus was of the order 0°.02 C during a run of about thirteen minutes and often no change in the Beckmann could be detected in this interval although it read directly to one hundredth of a degree.

It is interesting to note the continued increase in the stiffness of the steel suspension wire previously noted by Van Dyke. The suspension used was the "*F*" suspension of Harrington. The record of this change, indicated by the decreasing period, is as follows:

Harrington	175.58 sec.
Stacy	175.48 "
Van Dyke (Nov. 1920)	175.45 "
" " (June 1921)	175.42 "
States (April 1922)	175.25 "

Experimental Procedure

In a preceding paper Van Dyke has given the working equations and the general experimental procedure for the determination of the coefficients of viscosity and slip by the constant deflection method. It will be sufficient, therefore, to indicate the departures from this method.

Prior to the first slip work on oxygen the apparatus was allowed to stand several days at a pressure in the neighborhood of 0.001 mm of mercury after which it was bathed out and oxygen admitted to the chamber. Several determinations of apparent viscosity were made at about 6.5 cm of mercury. These were corrected for slip. The apparatus was then evacuated to a lower pressure, several apparent viscosity runs taken, which together with the mean of the former readings yielded values of ζ_{76}. The pumping was continued and more slip determinations made at this lower pressure. The process was continued until pressures were reached at which the mean free path of the molecules became comparable with the distance between the cylinders where the equations referred to do not hold. (See Tables I. and II.) The same method was

TABLE I. *Oxygen—First Sample. Coefficient of Slip—Unpolished Oxide Surface*

$\eta_{23} = 2035.8 \times 10^{-7}$, $k' = 8.1879 \times 10^{-7}$, $k = 2.814$

T = time from initial pumping to end of run

t (sec)	d (cm)	$\theta°$ C	p (mm)	$(\eta_0/\eta_p - 1) \times 10^3$	$\zeta_{76} \times 10^7$	T (hr)
30.394	77.954	22.826	0.274	48.9	62.7	1
30.442	77.872	22.805	0.274	48.3	61.9	1.33
30.416	77.991	22.820	0.274	47.7	61.1	1.75
30.430	77.993	22.985	0.277	47.6	61.7	18
30.415	78.090	23.100	0.278	47.2	61.4	18.5
30.426	76.746	23.200	0.196	65.4	60.0	19
30.413	76.717	23.040	0.196	65.8	60.3	23
30.389	76.847	23.107	0.196	65.0	59.6	23.5
30.394	76.527	22.820	0.196	68.4	62.7	41.5
30.388	76.579	22.859	0.196	68.0	62.3	42
30.401	76.552	22.795	0.196	67.7	62.1	46
30.400	76.619	22.839	0.196	67.0	61.4	46.5
30.388	76.834	23.204	0.196	65.5	60.0	61.0
30.382	76.735	23.192	0.196	67.1	61.5	61.5

Mean $\zeta_{76} = 61.3 \times 10^{-7}$

used in getting the viscosity of helium, the pressure being 10 cm of mercury instead of 6.5 cm. In the slip determinations, however, in order to save the helium, the gas was withdrawn after the viscosity runs by means of a Toepler pump, and then small quantities of helium were re-introduced into the apparatus for the low pressure observations. The method used on oxygen was tested and yielded the same value for the slip as the latter method. Furthermore, re-introducing the helium gave the same value of the coefficient of viscosity, which justified the use of the same value of η_0 for all slip computations. (See Tables III. and IV.) The slip observations for the polished oxide surface were taken

TABLE II. *Oxygen—Second Sample. Coefficient of Slip—Unpolished Oxide Surface*
$\eta_{23} = 2037.4 \times 10^{-7}$, $k' = 8.1879 \times 10^{-7}$, $k = 2.814$

t (sec)	d (cm)	$\theta°$ C	p (mm)	$(\eta_0/\eta_p - 1) \times 10^3$	$\zeta_{76} \times 10^7$	T (hr)
30.471	78.827	22.794	0.372	35.4	61.6	4.25
30.438	78.908	22.810	0.372	35.5	61.8	4.5
30.394	78.468	23.045	0.297	43.5	60.4	6.5
30.406	78.423	23.052	0.297	43.7	60.7	7.0
30.374	78.504	23.008	0.297	43.6	60.6	10
30.392	78.466	23.039	0.297	43.6	60.6	10.5
30.362	77.257	23.030	0.211	60.9	60.1	11.5
30.301	77.394	23.000	0.211	61.1	60.3	12
30.238	74.806	23.280	0.128	100.9	60.4	29.5
30.238	74.808	23.224	0.128	100.7	60.3	30
30.270	71.070	22.775	0.0848	155.9	61.8	52.5
30.248	71.184	22.742	0.0852	154.9	61.7	53

Mean $\zeta_{76} = 60.9 \times 10^{-7}$

in the same manner, with the exception that the apparatus was not allowed to stand at low pressures more than twenty-four hours but was evacuated to 0.0007 mm of mercury before the gas was introduced.

TABLE III. *Viscosity of Helium—Unpolished Oxide Surface*
$p = 10.0$ cm, $k' = 8.1879 \times 10^{-7}$

t (sec)	d (cm)	$\theta°$ C	$\eta_\theta \times 10^7$	$\eta_{23} \times 10^7$
30.482	78.554	22.790	1960.6	1961.6
30.450	78.654	22.820	1961.0	1961.8
30.462	78.635	22.875	1961.3	1961.9
30.476	78.593	22.890	1961.2	1961.7
30.541	78.421	22.890	1961.0	1961.5
30.512	78.520	22.902	1961.6	1962.0

Mean $\eta_{23} = 1961.8 \times 10^{-7}$
Corrected for slip, $\eta_{23} = 1962.3 \times 10^{-7}$

Instead of making an absolute determination of the coefficient of viscosity, several observations were made on the values of t the period of rotation, and d the corresponding deflection for air, just after the work on helium, and the value of $k' = \eta/td$ was calculated assuming the value of η_{23} for air to be 1822.6×10^{-7}, as determined by Harrington. The mean value of eight such observations gave $k' = (8.1879 \pm 0.0018) \times 10^{-7}$. The value of k' obtained some months before came out 0.1 per cent lower. This change was probably due to the decrease in the period of vibration of the inner cylinder which was of the order of one part in two thousand and effective in increasing k' by one part in one thousand. On account of this shift, the k' determined just after the helium runs

TABLE IV. *Helium. Coefficient of Slip—Unpolished Oxide Surface*

T' = time from introduction of gas to end of run

$\eta_{23} = 1962.3 \times 10^{-7}$, $k' = 8.1879 \times 10^{-7}$, $k = 2.814$

t (sec)	d (cm)	θ° C	p (mm)	$(\eta_0/\eta_p - 1) \times 10^3$	$\zeta_{76} \times 10^7$	T' (hr)
30.314	77.703	23.173	1.50	17.9	126	0.5
30.290	77.744	23.150	1.50	18.1	127	1.0
30.234	77.861	22.942	1.50	17.9	126	5
30.257	77.802	22.960	1.50	18.0	126	24
30.208	77.386	22.920	1.05	25.0	123	0.33
30.185	75.574	23.087	0.518	50.8	123	0.6
30.175	75.715	23.150	0.518	49.4	120	1
30.284	75.383	23.043	0.520	49.9	121	18.5
30.230	74.741	22.910	0.435	60.5	123	1.25
30.244	74.816	22.975	0.435	59.1	120	2
30.297	73.367	23.070	0.333	78.4	122	25
30.211	73.511	23.032	0.333	79.0	123	48

Mean $\zeta_{76} = 123 \times 10^{-7}$

was used in getting the value of the coefficient of viscosity of helium. In fact this value was used throughout the first work as the value of the slip is independent of k'. Another determination of k' was made after the oxide surface was polished and the cylinders re-set. The mean of six observations gave $k' = (8.1933 \pm 0.0015) \times 10^{-7}$.

TABLE V. *Oxygen. Coefficient of Slip—Polished Surface*

$\eta_{23} = 2036.0 \times 10^{-7}$, $k' = 8.1933 \times 10^{-7}$, $k = 2.814$

t (sec)	d (cm)	θ° C	p (mm)	$(\eta_0/\eta_p - 1) \times 10^3$	$\zeta_{76} \times 10^7$	T (hr)
30.384	77.438	23.060	0.250	56.3	65.7	1.5
30.384	77.477	23.062	0.251	55.8	65.7	2
30.344	75.732	23.078	0.170	81.5	64.9	3
30.326	73.759	23.155	0.121	112	63.5	3.5
30.223	71.197	23.160	0.0865	156	63.2	4
30.217	71.243	23.140	0.0884	155	64.2	4.5

Mean $\zeta_{76} = 64.5 \times 10^{-7}$

The temperature corrections were made using the following approximate formulæ for small variations in temperature about 23° C, the last two deduced from Sutherland's equation.

Air

$$\eta_\theta = \eta_{23} + 4.93(\theta - 23) \times 10^{-7}. \quad (2)$$

Oxygen

$$\eta_\theta = \eta_{23} + 5.54(\theta - 23) \times 10^{-7}. \quad (3)$$

Helium

$$\eta_\theta = \eta_{23} + 4.70(\theta - 23) \times 10^{-7}. \quad (4)$$

TABLE VI. *Helium. Coefficient of Slip—Polished Surface*

$\eta_{23} = 1962.3 \times 10^{-7}$, $k' = 8.1933 \times 10^{-7}$, $k = 2.814$

t (sec)	d (cm)	$\theta°$ C	p (mm)	$(\eta_0/\eta_p - 1) \times 10^3$	$\zeta_{76} \times 10^7$	T' (hr)
29.911	78.486	22.982	1.74	20.1	164	0.33
29.840	78.673	23.038	1.74	20.3	165	0.75
30.484	76.909	22.858	1.62	21.2	161	17
29.952	78.303	23.102	1.60	21.4	160	0.5
29.985	78.242	23.130	1.60	21.2	159	1
30.431	76.394	23.146	1.11	30.6	159	2
30.392	76.489	23.145	1.11	30.6	159	2.5
30.370	74.398	23.155	0.552	60.4	156	3
30.253	72.634	22.895	0.373	89.7	157	19
30.080	73.071	22.915	0.373	89.4	156	19.5

Mean $\zeta_{76} = 160 \times 10^{-7}$

The constant for oxygen is Sutherland's value; that for helium is Schmitt's. The Eq. (2) is the one used by Prof. Millikan.[1]

THE GASES

Oxygen.—The oxygen for the coefficient of slip determinations was obtained by heating potassium permanganate. The flask containing the permanganate was heated a number of times and after each heating the flask and connecting tubing was exhausted to the point where a discharge passed outside rather than through a Geissler tube. The heat drove out the occluded gases from the flask and at the same time the liberated oxygen washed out the auxiliary apparatus. Heat was then applied and the oxygen produced was admitted to the large volume enclosing the cylinders through a coil made from a meter and a half of tubing in series with two traps, all at liquid air temperatures. This process gave quite pure oxygen, free from carbon dioxide and moisture, but showing hydrogen as an impurity when examined by a spectroscope using a disruptive discharge. However, the gas gave a coefficient of viscosity only 0.3 per cent lower than the value obtained by Yen [2] on the same apparatus when very pure oxygen was used. In view of this, and coupled with the fact that η_{23} for hydrogen is about one third of η_{23} for oxygen, little hydrogen could have been present. Furthermore, one would expect slight impurities not to affect the value of the coefficient of slip in as much as the determining quantity is a ratio of two apparent coefficients of viscosity of the same gas at different pressures, the percentage of impurities being nearly constant. Within the limit of experimental error, the values of the coefficient of slip (unpolished oxide surface)

[1] Millikan, Ann. der Phys. **41**, 759 (1913).

[2] Yen, Phil. Mag. **38**, 582 (1919).

of the two samples of oxygen are the same, although the viscosities of the two samples differ. This seems to justify the assumption that slight impurities do not affect the coefficient of slip.

Helium.—The helium, approximately 97–98 per cent pure, was obtained from the laboratory supply. The chief impurities were nitrogen, oxygen, hydrogen, neon and possibly some hydro-carbons. This gas was circulated through charcoal tubes at liquid air temperatures by means of a Toepler pump, a process which removed most of the impurities. A copper oxide tube removed the hydrogen. This purified gas, examined with a spectroscope and under a disruptive discharge, showed a trace of hydrogen and neon at favorable pressures. Collie and Ramsay [1] found that 0.001 per cent of hydrogen was visible in helium at all pressures and obtained similar results for inert gases in helium. Gille [2] found that one per cent of hydrogen lowered the viscosity of helium less than one per cent. In this instance there could be no such amount present. In view of this, the slight trace of hydrogen and neon present would introduce a negligible error. It might be stated that the process of purification was continued until no change in the viscosity was apparent, and that the last set of readings is given in Table III. The values just previous to these, in which a change was noted, indicated that neon was the last impurity taken up by the charcoal.

Discussion

The value of the coefficient of viscosity of helium here recorded is lower than that usually quoted. Determinations by the capillary tube method, however, generally yield values somewhat higher than those obtained by the constant deflection method. The ratios of values of viscosity usually come out about the same. In this instance the ratios disagree by nine parts in one thousand. Using Harrington's value of air, we have η_{23} (He) = 1.077 η_{23} (air). Shultz [3] using the capillary tube method got η_{15} (He) = 1.086 η_{15} (air), which ratio would not be materially changed at 23° C in as much as the temperature coefficients of the two gases are nearly the same. Rankine [4] using a modified form of the capillary tube method got $\eta_{9.8}$ (He) = 1.078 $\eta_{9.8}$ (air). After making an approximate slip correction his value agrees with Shutlz's. Shultz's value of the coefficient of viscosity of helium at 15° C, reduced by the Sutherland formula, gives η_{23} (He) = 2006×10^{-7}.

In spite of this the writer feels justified in claiming a high degree of

[1] Collie and Ramsay, Roy. Soc. Proc. **59**, 257 (1896).
[2] Gille, Ann. der Phys. **48**, 829 (1915).
[3] Shultz, Ann. der Phys. **6**, 302 (1901).
[4] Rankine, Roy. Soc. Proc. **83**, 516 (1910).

precision for the value of the coefficient of viscosity of helium obtained. The method itself is generally considered to be superior to the capillary tube method. A statement as to the purity of the gas has already been made. Finally, from the small probable error in the mean value of k' and from the consistency in the values of η_{23} for helium, it would appear that the value quoted is as nearly correct as Harrington's value of η_{23} for air. The error in Harrington's work is probably not more than 0.1 per cent.

As has been pointed out, the coefficient of slip is essentially a difference between two measured physical quantities, each of which involves an error of the order of 0.1 per cent. When this difference is small, the error in the value of the slip may amount to several per cent. On the other hand, when the difference is large, the error mentioned would be small, but since the pressure for one of the readings would have to be low, the value of the slip coefficient would be unreliable, for at low pressures the free path becomes comparable with the distance between the cylinders. For this reason the slip determinations here recorded were taken within a range of pressures where the two effects taken together would introduce the least distortion. The range of pressures for oxygen was between 0.37 mm and 0.08 mm of mercury. For helium, the free path being approximately three times that of oxygen, the range of pressures was shifted to values about three times as high. The mean of the coefficients of slip within this limited range should be correct to within one per cent.

The fact that the "time effect" was not observed in the slip work is largely responsible for the consistency in the values of ζ_{76}. Stacy and Van Dyke usually disregarded readings after the first hour or two, due to the *rise* in slip. This increase was attributed to the release of occluded gases of low viscosity. In trying out the silver oxide with air, the "time effect" was marked, but in the *reverse* direction. Silver oxide was found to give off oxygen at low pressures which would account for this decrease. In order to make sure that this was the true cause of the "time effect," a study was made of the coefficient of slip of oxygen, which ought to remain constant with time upon the above hypothesis. Tables I., II., and V. indicate slight changes in pressure but constant values of the slip, which seems to verify the contention. In view of this, the mean value of ζ_{76} is probably equal to the value of the coefficient of slip at zero time.

In helium no "time effect" was observed. This may be due to the fact that the coefficients of viscosity of helium and oxygen are nearly the same. Before the first helium runs were taken, however, the apparatus stood for a month at a pressure of about 0.001 mm of mercury. In the later slip work, the apparatus stood at low pressures for about 24 hours

and, as before stated, was evacuated to a pressure of the order of 0.0007 mm of mercury before the helium was introduced; consequently over a range of pressures from 1.7 mm to 0.33 mm of mercury one might not expect the release of oxygen. A combination of these two effects may account for the consistency in the values of ζ_{76}.

The coefficients of slip of oxygen and helium obtained are considerably lower than any values which might be expected from Maxwell's expression for slip. The minimum value given by Eq. (1) would be obtained by imposing the condition of diffuse reflection; *i.e.*, placing $f = 1$. Whence ζ_{76} for oxygen $= 70 \times 10^{-7}$ and ζ_{76} for helium $= 191 \times 10^{-7}$. The viscosities of oxygen and helium are so high in comparison with the viscosities of gases or vapors which might reasonably be expected to enter as impurities at low pressures that lowering of the slip through an increase of viscosity seems improbable. The observations seem to indicate no measurable change in slip over intervals as long as sixty hours, which would hardly be expected if there were changes in the character of the gas at low pressures. Turning to surface conditions, diffuse reflection would mean that the entire tangential component of the momentum per second due to the streaming velocity of the molecules is communicated to the surface. A lower value of the slip could arise only when a larger tangential force exists at the surface. This condition would be satisfied if a part of the molecules striking the surface rebounded with a component of velocity opposite to the general streaming velocity, the remainder of the molecules being assumed diffusely reflected. This abnormal tangential force also suggests an increased density at the bounding surface, the excess molecules being furnished by the oxide surface. This would tend to diminish the streaming velocity of the surface layer and thereby increase the force at the surface of the cylinders.

In conclusion, the writer wishes to thank Professor R. A. Millikan for suggesting this further study of the slip, and Professor H. G. Gale and other members of the staff at Ryerson for helpful suggestions and assistance in various phases of the work, especially in the purification and analysis of the gases.

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THE STATISTICAL THEORY OF SPONTANEOUS FLUCTUATIONS IN ENERGY, PRESSURE, AND DENSITY.

By Kulesh Chandra Kar.

Abstract.

Theoretical derivation of expressions for fluctuations in energy, pressure, and density.—The fluctuation of a quantity, such as the energy, is defined as the ratio of the average deviation from the mean energy to the mean energy. The following expressions are deduced from a new statistical theory for ordinary temperature and pressure: Fluctuation in energy at constant volume $= \sqrt{(2/\gamma nf)}$ and at constant temperature $= 2/f\sqrt{n}$; Fluctuation in pressure or density at constant temperature $= 1/\sqrt{n}$; where n is the number of molecules, f the number of degrees of freedom of each, and γ the ratio of total energy to kinetic energy. At the critical condition the first of these becomes $(12/\gamma nf)^{1/4}$ and the last $(6/n)^{1/4}$. The expressions obtained by Smoluchowski, Hauer, Fürth and Laue are shown to be special cases of the above. Relations are obtained between the various types of fluctuations for the case of an ideal gas.

Introduction.

In 1904 Smoluchowski [1] obtained from theoretical considerations the equation for the mean isothermal fluctuation of density of a gas $|\bar{\delta}_e|_T$ due to molecular collisions

$$|\bar{\delta}_e|_T = \sqrt{\frac{2}{\pi n}} = \frac{.797}{\sqrt{n}}, \tag{1}$$

where n is the number of molecules inside the volume considered.

This equation being true for a gas will also hold for colloidal particles. As a result of a series of observations [2] with colloidal solutions Svedberg, Westgren and others found that the fluctuation of density really obeys Smoluchowski's equation.

In 1908 Smoluchowski [3] showed that at the critical condition of a gas $|\bar{\delta}_e|_T$ is given by the equation

$$|\bar{\delta}_e|_T = \frac{1.13}{\sqrt[4]{n}}, \tag{2}$$

which was subsequently verified by Kammarlingh Onnes and Keesom.[4] Thus at the critical state the mean fluctuation is greater than at the ordinary condition. Smoluchowski, however, suggested that this fluc-

[1] Boltzman, Festschrift, s. 626 (1904).
[2] Svedberg, Die Existenz der Moleküle, Leipzig, 1912.
[3] Ann. d. Phys., 25, 205 (1908).
[4] Comm. fr. the Phys. Lab. of Leiden (1908).

tuation of density might give rise to opalescence noticeable at the critical state of a gas. But he did not in that paper obtain any expression for the intensity of the opalescent light. Subsequently in 1910 Einstein [1] obtained the value of the mean intensity of opalescent light which agreed with Keesom's [2] equation found experimentally on working with ethylene at its critical condition. It is noteworthy that in deducing the equation Einstein supposed the variation of density to be a circular function of the coördinates. Now the intensity of opalescent light [3] as calculated from Smoluchowski's equation is exactly the same as that from Einstein's equation putting $\phi = 0$. This is again an indirect verification of Smoluchowski's equation (2).

Later in 1915 F. v. Hauer [4] obtained an expression for the isochoric temperature fluctuation of an ideal gas at the ordinary conditions.

$$(3) \qquad (\overline{\delta_T{}^2})_v = 2/3n.$$

More recently, however, M. v. Laue [5] and R. Fürth [6] have found the energy and pressure fluctuations by a somewhat similar method.

$$(4) \qquad \overline{\delta_u{}^2} = \frac{KT_0v_0}{\Delta v \cdot \overline{U}^2}\left\{ -\frac{(d\overline{U}/dv)^2}{(dp/dv)} + C_vT_0 \right\} \qquad \text{(Laue)},$$

$$(5) \qquad \overline{\delta_p{}^2} = x/n \quad \text{where} \quad x = C_p/C_v \qquad \text{(Fürth)}.$$

It should be noted, however, that in these two kinds of fluctuations the temperature and volume are not constant.

In the present paper it is proposed to develop a statistical theory of the different kinds of fluctuations.

Statistical Theory.

Let us consider a volume containing n molecules within a large volume of a gas and suppose each molecule has f degrees of freedom. Then the behavior of the gas in the volume considered is given at any instant by the position of the representative point in $2nf$ dimensional phase space. Now due to molecular collisions and other factors, the representative point does not move in the same energy surface U_0 but between two energy surfaces U_0 and $U_0 + dU_0$. Or in other words the representative points are canonically distributed in Gibbs's phase space according to

[1] Ann. d. Phys., 33, 1294 (1910).

[2] Ann. d. Phys., 35, 591 (1911).

[3] Die Theorie der Strahlung und der Quanten, von A. Eucken, p. 182, W. Knapp (1914).

[4] Hauer, Ann. der Phys. 47, 365, 1915.

[5] Laue, Phys. Zeit. 18, 542, 1917; also R. Fürth, Schwankungserscheinungen in der Physik.

[6] Fürth, Phys. Zeit. 20, 350, 1919.

the equation [1]

$$\epsilon = Ne^{\frac{\psi - U}{\theta}},$$

where U is the energy.

Thus in the canonical distribution the energy of the representative point does not remain constant but fluctuates within a certain range. And this fluctuation of energy, or the "dispersion of energy" as it is generally called, of the representative point measures the variation of energy of the n molecules which it represents. If we suppose the potential energy of the molecules to be nothing, the fluctuation of energy of the molecules can be caused only by the dispersion in the velocity or the positional space. Thus the total dispersion of energy is equal to the sum of the two partial dispersions in the velocity and the positional space. And it is evident that the energy fluctuation, when there is no dispersion in the positional space (Lagenraum), will correspond to the energy or temperature fluctuation at constant volume (Hauer). Then again the fluctuation of energy at constant velocity space will give rise to pressure fluctuation at constant temperature. But they will not be identical as will be discussed below. Now let us calculate the energy or the temperature fluctuation at constant volume from the dispersion theory.

We have for the fluctuation of energy, $(U - \overline{U})/\overline{U}$.

Suppose

$$U = \overline{U} + \xi;$$

therefore

$$U^2 = (\overline{U})^2 + \xi^2 + 2\xi \cdot \overline{U}.$$

Taking the mean and remembering that $\bar{\xi} = 0$ we have

$$\overline{\xi^2} = \overline{U^2} - (\overline{U})^2;$$

therefore

$$\bar{\delta}_u^2 = \frac{\overline{U^2} - (\overline{U})^2}{(\overline{U})^2}.$$

Also:

$$\overline{U} = \frac{\int U e^{-\frac{U}{\theta}} \Delta\tau}{\int e^{-\frac{U}{\theta}} \Delta\tau},$$

$$\overline{U^2} = \frac{\int U^2 e^{-\frac{U}{\theta}} \Delta\tau}{\int e^{-\frac{U}{\theta}} \Delta\tau},$$

where $\Delta\tau = \Delta\tau_p \cdot \Delta\tau_q$.

[1] C. Shaefer, Einführung in die theoretische Physik, Bd. II., Berlin, 1921; also Gibbs, Statistical Mechanics.

(6) Putting x for $1/\theta$ and P for $\int e^{-\frac{U}{\theta}}\Delta\tau$ or $\int e^{-U_z}\Delta\tau$, we have

$$\overline{U} = -\frac{1}{P}\frac{dP}{dx}, \tag{7}$$

$$\overline{U^2} = \frac{1}{P}\frac{d^2P}{dx^2}. \tag{8}$$

Therefore

$$\overline{\xi^2} = \overline{U^2} - (\overline{U})^2 = \frac{1}{P}\frac{d^2P}{dx^2} - \frac{1}{P^2}\left(\frac{dP}{dx}\right)^2$$

$$= \frac{d}{dx}\left(\frac{\frac{dP}{dx}}{P}\right).$$

Hence remembering (7)

$$\overline{\xi^2} = -\frac{d\overline{U}}{dx}$$

$$= \theta^2\frac{d\overline{U}}{d\theta} \text{ from (6).}$$

Suppose $\overline{U} = \gamma L$,[1] $\overline{L}$ being the kinetic energy. From the equipartition theorem

$$\overline{U} = \frac{\gamma nf}{2}\theta, \tag{9}$$

so that

$$\overline{\xi^2} = \frac{\gamma nf}{2}\theta^2.$$

Hence

$$(\overline{\delta}_u^2)_v = \frac{2}{\gamma nf}$$

or

$$|\overline{\delta}_u|_v = \sqrt{\frac{2}{\gamma nf}}.$$

For ideal gas or colloidal particles $\gamma = 1$ and $f = 3$, thus, at ordinary temperature and pressure,

$$|\overline{\delta}| = \sqrt{\frac{2}{3n}} = \frac{.816}{\sqrt{n}},$$

which is Hauer's equation.

At the critical condition we suppose $\overline{\xi^2} = 0$, so

$$\overline{\delta}_u^4 = \frac{\overline{\xi^4}}{(\overline{U})^4} = \frac{\overline{U^4} - (\overline{U})^4}{(\overline{U})^4}. \tag{10}$$

[1] For an ideal gas, the potential energy ϕ is zero, so that $\gamma = 1$, but for solids $\overline{\phi} = \overline{L}$, *i.e.*, $\gamma = 2$.

Differentiating (7) with respect to x we have

$$\frac{d}{dx}(\overline{U}) = \frac{-\frac{d^2P}{dx^2}}{P} + \frac{\left(\frac{dP}{dx}\right)^2}{P^2}. \tag{11}$$

On further differentiation with respect to x

$$\frac{d^2}{dx^2}(\overline{U}) = \frac{-\frac{d^3P}{dx^3}}{P} + 3\frac{dP}{dx}\cdot\frac{d^2P}{dx^2} - \frac{2\left(\frac{dP}{dx}\right)^3}{P^3}. \tag{12}$$

On differentiating again

$$\frac{d^3}{dx^3}(\overline{U}) = \frac{-\frac{d^4P}{dx^4}}{P} + 4\cdot\frac{\frac{d^3P}{dx^3}\cdot\frac{dP}{dx}}{P^2} + 3\frac{\left(\frac{d^2P}{dx^2}\right)^2}{P^2} - 12\frac{\left(\frac{dP}{dx}\right)^2\frac{d^2P}{dx^2}}{P^3} + 6\frac{\left(\frac{dP}{dx}\right)^4}{P^4}. \tag{13}$$

Substituting the value of $\overline{U}$ from (9) in (11) remembering (8)

$$\begin{aligned}\overline{U^2} &= \theta^2\frac{d\overline{U}}{d\theta} + (\overline{U})^2 \\ &= \frac{\theta^2\gamma nf}{2}\left(1 + \frac{\gamma nf}{2}\right).\end{aligned} \tag{11a}$$

Again substituting values of $\overline{U^2}$ and $\overline{U}$ in (12) we have

$$\begin{aligned}-\overline{U^3} &= -\theta^3\gamma nf + \frac{3}{4}\theta^3\gamma^2n^2f^2\left(1 + \frac{\gamma nf}{2}\right) - \frac{\gamma^3n^3f^3\theta^3}{4} \\ &= \theta^3\gamma nf\left\{-1 + \frac{3}{4}\gamma nf\left(1 + \frac{\gamma nf}{2}\right) - \frac{\gamma^2n^2f^2}{4}\right\}.\end{aligned} \tag{12a}$$

Similarly from (13)

$$\begin{aligned}\overline{U^4} &= 3\theta^4\gamma nf + 2\gamma nf\theta\cdot\theta^3\gamma nf\left\{-1 + \frac{3}{4}\gamma nf\left(1 + \frac{\gamma nf}{2}\right) - \frac{\gamma^2n^2f^2}{4}\right\} \\ &\quad + 3\cdot\frac{\theta^4\gamma^2n^2f^2}{4}\left(1 + \frac{\gamma nf}{2}\right)^2 \\ &\quad - 12\cdot\frac{\theta^2\gamma^2n^2f^2}{4}\cdot\frac{\theta^2\gamma nf}{2}\left(1 + \frac{\gamma nf}{2}\right) + 6\frac{\gamma^4n^4f^4\theta^4}{16}.\end{aligned} \tag{13a}$$

Therefore

$$\overline{\xi^4} = \overline{U^4} - (\overline{U})^4 = 3\theta^4\gamma nf + 2\theta^4\gamma^2n^2f^2\left\{-1 + \frac{3}{4}\gamma nf\left(1 + \frac{\gamma nf}{2}\right) - \frac{\gamma^2n^2f^2}{4}\right\}$$

$$+ 3\cdot\frac{\theta^4\gamma^2n^2f^2}{4}\left(1 + \frac{\gamma nf}{2}\right)^2 - 12\frac{\theta^4\gamma^3n^3f^3}{8}\left(1 + \frac{\gamma nf}{2}\right) + 5\cdot\frac{\gamma^4n^4f^4\theta^4}{16}$$

$$= \frac{3}{4}\gamma^3 n^3 f^3 \theta^4 - \frac{5}{4}\gamma^2 n^2 f^2 \theta^4 + 3\gamma n f \theta^4.$$

Hence

$$(\bar{\delta}_u^4)_v = \frac{\frac{3}{4}\gamma^3 n^3 f^3 \theta^4 - \frac{5}{4}\gamma^2 n^2 f^2 \theta^4 + 3\gamma n f \theta^4}{\frac{1}{16}\gamma^4 n^4 f^4 \theta^4}$$

$$= \frac{12}{\gamma n f} - \frac{20}{\gamma^2 n^2 f^2} + \frac{48}{\gamma^3 n^3 f^3}$$

$$= \frac{12}{\gamma n f}$$

when n is large or

$$|\bar{\delta}_u|_v = \sqrt[4]{\frac{12}{\gamma n f}}.$$

For simplicity we suppose $\phi = 0$ or $\gamma = 1$, so that

$$|\bar{\delta}_u|_v = \sqrt[4]{\frac{12}{n f}}. \tag{14}$$

Let us now find the pressure fluctuation at constant temperature. As before we have the isothermal pressure fluctuation at ordinary conditions given by

$$(\overline{\delta_p^2})_T = \frac{\overline{p^2} - (\bar{p})^2}{(\bar{p})^2}. \tag{15}$$

Also:

$$\bar{p} = \frac{\int (dU/dv) e^{-U/\theta} \Delta\tau}{\int e^{-U/\theta} \Delta\tau},$$

[1]

$$\overline{p^2} = \frac{\int (dU/dv)^2 e^{-U/\theta} \Delta\tau}{\int e^{-U/\theta} \Delta\tau}.$$

Remembering (6) we have

$$\frac{dP}{dv} = -\frac{1}{\theta}\int \frac{dU}{dv} e^{-U/\theta} \Delta\tau,$$

$$\frac{d^2P}{dv^2} = +\frac{1}{\theta^2}\int \left(\frac{dU}{dv}\right)^2 e^{-U/\theta} \Delta\tau.$$

Hence we have

$$\bar{p} = -\theta \frac{dP/dv}{P},$$

$$\overline{p^2} = +\theta^2 \frac{d^2P/dv^2}{P}. \tag{16}$$

Substituting (16) in (15) and after transformation we get

[1] C. Schaefer, loc. cit., p. 445 (85).

$$(17) \qquad (\overline{\delta_p{}^2})_T = \theta^2 \frac{d}{dv}\left(\frac{dP/dv}{P}\right) \Big/ (\bar{p})^2 = -\theta \frac{d\bar{p}/dv}{(\bar{p})^2};$$

$$(18) \qquad \text{but } \bar{p} = n\theta/v.^1$$

Using (18) we get

$$(19) \qquad (\overline{\delta_p{}^2})_T = 1/n.$$

Now at the critical condition, dp/dv in (17) is zero, so that $(\overline{\delta_p{}^2})_T = 0$. Therefore the critical fluctuation of pressure will be given by

$$(20) \qquad (\overline{\delta_p{}^4})_T = \frac{\overline{p}^4 - (\bar{p})^4}{(\bar{p})^4}.$$

The right-hand term of equation (20) is evaluated as in (10) and we have

$$(\overline{\delta_p{}^4})_T = \frac{6}{n} + \frac{11}{n^2} + \frac{6}{n^3},$$

or when n is large

$$(21) \qquad (\overline{\delta_p{}^4})_T = 6/n, \text{ i.e. } |\bar{\delta}_p|_T = 1{\cdot}56/\sqrt[4]{n}.$$

One may note here that the iosthermal energy fluctuation cannot be obtained as the isothermal pressure fluctuation. Therefore a special device has been used in this case. It is not difficult to see that equation (17), in which p is taken only as a function of volume, is perfectly general and it will be possible to get the value of $(\overline{\delta_u{}^2})_T$ by simply putting U for p. We thus have from (17)

$$(\overline{\delta_u{}^2})_T = -\theta \frac{d\bar{U}}{dv} \Big/ (\bar{U})^2 = -\theta \frac{\bar{p}}{(\bar{U})^2}.$$

Now remembering $\bar{U} = (f/2)(n\theta/v)$ and $\bar{p} = n\theta/v$, we have

$$(22) \qquad (\overline{\delta_u{}^2})_T = 4/f^2 n.$$

We leave the matter here to discuss it later on in connection with Laue's energy fluctuation.

Relation Between Different Kinds of Fluctuation.

After deducing from the dispersion theory the values of $(\overline{\delta_u{}^2})_v$, $(\overline{\delta_T{}^2})_v$, $(\overline{\delta_u{}^2})_T$ and $(\overline{\delta_p{}^2})_T$, we shall next proceed to find the different kinds of fluctuations considered by previous workers referred to in the introduct on, from the fundamental relation proved just now.

From the gas equation $pv = RT$ we have

$$(p^2 + \overline{\Delta p^2})(v^2 - \overline{\Delta v^2}) = R^2(T^2 + \overline{\Delta T^2}),$$

where the bar represents the mean fluctuation of the corresponding quantities.

[1] C. Schaefer, loc. cit., p. 447 (98).

(23) $$\text{Hence } \frac{\overline{\Delta p^2}}{p^2} - \frac{\overline{\Delta v^2}}{v^2} = \frac{\overline{\Delta T^2}}{T^2}.$$

From the above equation we get the following fundamental relations:

(24a) $$(\overline{\delta_p{}^2})_T = (\overline{\delta_v{}^2})_T,$$

(24b) $$(\overline{\delta_p{}^2})_v = (\overline{\delta_T{}^2})_v,$$

(24c) $$(\overline{\delta_v{}^2})_p = -(\overline{\delta_T{}^2})_p,$$

(24d) $$\overline{\delta_v{}^2} = \overline{\delta_\rho{}^2},$$

where ρ is the density.

Now combining (24a) and (24d) we have

$$(\overline{\delta_p{}^2})_T = (\overline{\delta_\rho{}^2})_T$$

and hence with the help of (19) we have

(25) $$(\overline{\delta_\rho{}^2})_T = 1/n,$$

which is Smoluchowski's density fluctuation.[1]

Again we have the general equation

$$\overline{\delta_p{}^2} = (\overline{\delta_p{}^2})_T + (\overline{\delta_p{}^2})_v.$$

Now using (24b) we have

$$\overline{\delta_p{}^2} = (\overline{\delta_p{}^2})_T + (\overline{\delta_T{}^2})_v = (\overline{\delta_p{}^2})_T + (\overline{\delta_u{}^2})_v,$$

or substituting the values of terms in the right-hand side of the equation we get

$$\begin{aligned}\overline{\delta_p{}^2} &= 1/n + 2/fn \\ &= x/n \quad \text{where} \quad x = (f+2)/f,\end{aligned}$$

and this is Fürth's equation (5) for pressure fluctuation at the ordinary conditions. And at the critical state this fluctuation will be $6x/n$ as will be seen from (14) and (21).

Similarly we have for the energy fluctuation

$$\begin{aligned}\overline{\delta_u{}^2} &= (\overline{\delta_u{}^2})_v + (\overline{\delta_u{}^2}). \\ &= 2/fn + 4/f^2n = 2x/fn,\end{aligned}$$

this being Laue's equation as will be seen by transforming his original equation (4) with the help of the well-known formulæ

$$\frac{d\overline{U}}{dv} = \overline{p} = \frac{nkT}{v}, \quad \text{where} \quad kT = \theta,$$

$$\overline{U} = (f/2)(nkT/v) \quad \text{and} \quad c_v = (f/2)(nk/v).$$

47 CORPORATION STREET,
CALCUTTA, March 29, 1923.

[1] In his paper referred to in the introduction, Smoluchowski has calculated $|\bar{\delta}_\rho|_T$ and not $(\overline{\delta_\rho{}^2})_T$. But $(\overline{\delta_\rho{}^2})_T$ calculated from his theory is exactly as in (25). See Fürth, Schwankungserscheinungen, pp. 22 and 55.

THE EFFECT OF TEMPERATURE ON GRAVITATIVE ATTRACTION

By P. E. Shaw and N. Davy

Abstract

Variation of gravitational attraction with the temperature of the larger mass, 20° to 250° C.—It is invariably assumed in computing the masses of the heavenly bodies that the temperature effect is zero; but except for the work of the authors, we have no direct evidence for this assumption, since it must be allowed that the results of balance experiments in which the temperature of the smaller mass is varied up to 100° only are inconclusive. In 1915 a laborious series of experiments was performed with a Cavendish torsion balance, which indicated a positive temperature coefficient for the gravitational constant, of 10^{-5} per degree. Recently the apparatus has been changed by substituting a more rigid support, iron girders for the former wooden scaffolding, and by providing better thermal insulation between the heated outside large masses and the vacuum chamber containing the smaller masses. The result of eleven series of readings is a mean difference (hot minus cold deflection) of $-$ .05 mm in 208 mm, or 1/40 per cent on a range of 200°. While most of the differences are negative, two positive results were obtained; and since the observational error is of the same order as the result, the conclusion is that the effect, if it exists, is less than 2×10^{-6} per degree, and may well be zero. The previous result is explained as probably due to a slight change in the relative positions of the large and small masses, reversible with the temperature change.

Introduction

SOME years ago one of us published an account of experiments on this subject.[1] The results shown in that paper seemed to indicate that the attraction between masses depends, under certain conditions, on their temperature. The ultimate result attained in that research was that, on raising the temperature of the large external masses M, M, of a torsion balance system in which the small internal masses m, m remain at constant temperature, the attraction of the large on the small masses increases by about $1/10^5$ per 1° C.

In a later paper[2] it was shown as the result of further work that the above numerical result is increased about 8 per cent when allowance is made for expansion of the beam carrying the large masses. The above

[1] Shaw, Phil. Trans. (May, 1916). The text of this paper unfortunately contains a few errors of an important nature. For these we append the following errata: p. 356 Equation III should read: $\theta = CM^{1/3} \cdot D^{2/3}T^2/a$; p. 357 (line 9) should read: Sensitiveness $\propto$ R.D.; p. 357 (line 10) should read: Radius and Density are of equal importance; pp. 373, 375, 380: The oscillation periods should be 252, 280, 280 seconds (not minutes).

[2] Shaw and Hayes, Proc. Roy. Soc. (April, 1917).

temperature effect was obtained after eight years of work, mostly spent on overcoming the technical difficulties peculiar to the experiment.

This result is certainly important if true. Thus, the masses and densities of the earth, sun and planets and other heavenly bodies are all derived by supposing these bodies, though at very high mean temperatures, to have the same gravitative pull as if their temperatures were those of the masses used, say, in a laboratory in a Cavendish torsion balance at 20° C. And although in the experiments about to be described the temperature only rises to about 250° C at the most, whereas the mean temperature of the sun and stars may be reckoned in four or five figures on the Centigrade scale, yet any evidence of a temperature effect found at low scale temperatures would at once invalidate the commonly quoted figures for mass and density, and we should have to regard them at best as "effective" and not true values. In that case, since we can never deal experimentally with these very high temperatures, we could never hope to know the true masses of the heavenly bodies.

The *nil* effect obtained by Poynting and Phillips [3] and that of Southerns [4] do not directly affect the issue. They are both "weight" experiments made with a gravity balance and therefore directly deal with the small mass only, whereas the present research deals with the large mass. But even if it be claimed that these weight experiments provide an *a priori* proof that there is no temperature effect, this claim can only be made for temperatures up to 100° C, which was the upper limit used in these researches. Therefore we have no experimental warrant apart from the present series of researches for considering the Newtonian constant of gravitation to be unaffected by rise of temperatures above 100° C; and the present work only carries us up to 270° C.

Method and Apparatus

The general methods of the present research are identical with those employed before and the materials also are unchanged. But the supports and the suspending systems of the large masses M, M' and of the small masses m, m' are entirely different; they are stronger and more massive. It is clear from a study of the old experiments that even minute movements occurring during an experiment of the small masses relative to the large ones might cause spurious effects of the order of the small temperature effect found. So it was felt that in repeating the work special care should be taken to provide rigidity and immobility in these particulars. The changes introduced have greatly improved the apparatus and enabled a higher order of accuracy to be reached, and

[3] Roy. Soc. Proc. A, **76** (1905).
[4] Roy. Soc. Proc. A, **78** (1906).

it is now found that the temperature effect is less than 2×10^{-6} and may well be zero.

Of the apparatus and processes used only a brief account is required as they are similar to those given in detail in the former paper,[1] to which the reader is referred for a further account of methods and precautions employed. Stated in general terms, the object of the research is to measure the change in attraction, if any, occurring between two solid masses, one large and one small, when the temperature of the large one is raised. A torsion balance of the Boys-Cavendish type is employed. The torsion system carries the small masses in a vacuum, outside which are the large masses. Between the large and small masses screens are arranged to stop the flow of heat to the inner system from the large masses when these are raised in temperature.

The Inner System.—Figs. 1 and 2 are side and front views of the main part of the apparatus. In the center of Fig. 1 is the vacuum tube *VV* which is 120 cm long and 5 cm in diameter, and contains the torsion balance with its small suspended masses *m*, *m'*, hanging by separate wires, 32 mm apart. *VV* is suspended inside the sheath *S* by a cranked iron bar *D* supported on and swivelling in sleeves on a board *T*. This board is heavily loaded with lead *L* and is supported by 16 steel springs whose upper ends are attached to an iron frame *F* which is bolted in four places to the pair of stout angle irons *AG*. These irons stretch across the width of the vault and are recessed into the holes in the brick walls. They are heavily loaded and rest on steel balls which are imbedded in rubber pads *P*. Thus the angle irons and their attachments form a "floating" system free in part from the vibrations of the walls. The board *T* and the vacuum tube suspended from it in cantilever fashion form an *inner* floating system whose lateral movements are checked by rubber pads *R* resting on the angle irons while the tube *S* resting on the tripod *Tr* constitutes an *outer* system.

The lower end of the vacuum tube is firmly socketed into a brass tube which penetrates a brass ring *K* in which are four set-screws to adjust the tube to a plumb position and hold it there. The ring *K* is clamped to two piers of cemented bricks *Br* resting on concrete slabs *C*. The whole masonry base weighs 500 lb and rests on rubber blocks *Ru*. Thus the supports of the vacuum tube and its contents both above and below consist of heavy floating systems. In this way the torsion balance is well guarded from the tremors of the building and ground. These special anti-tremor devices are required by reason of the location of the apparatus in the University College in the center of Nottingham and near a trunk railway. In using an asymmetrical system such as this torsion

balance, which has the small masses at different heights, any tremors when once received are converted into pendular movements of two frequencies and thence into torsional vibrations. These vibrations are long retained but die away gradually by the viscous drag of the residual air in the vacuum.

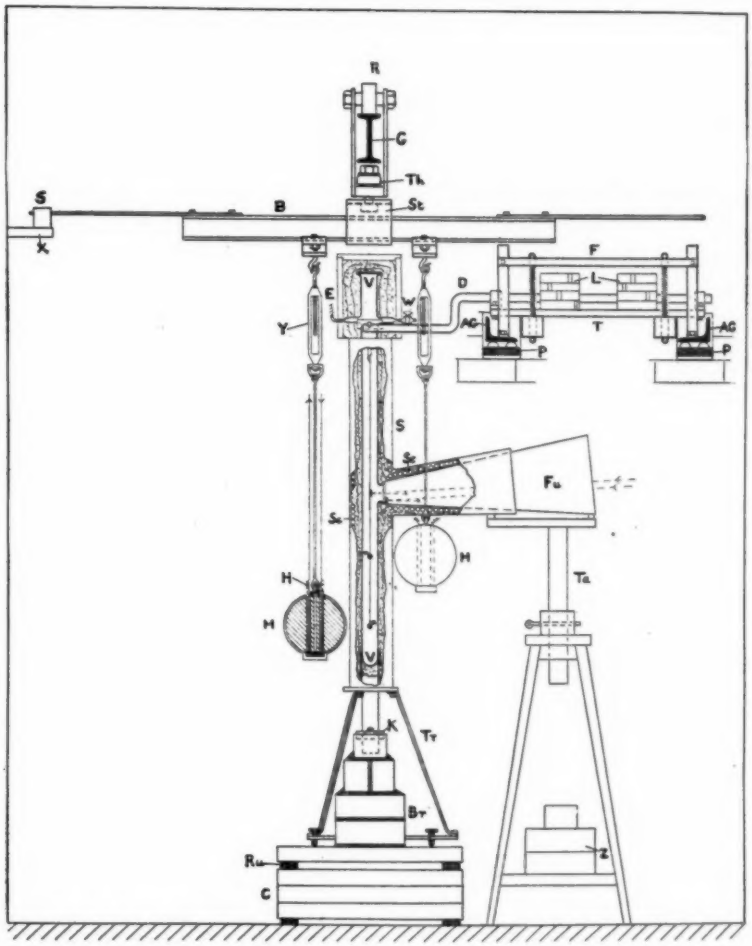

Fig. 1

At the top of the vacuum tube *VV* are seen the wire *E*, for earthing the inside of the tube, and the tap *W*, which is connected by tube *VT*, Fig. 2, to the vacuum pump and manometer. The vacuum tube is surrounded by cotton wool lagging, helical rubber water tubes, and polished copper sheath, as shown in Fig. 1, the whole forming a wall all round the vacuum tube, 4 cm thick, designed to maintain the temperature in the vacuum

constant even when the large external masses M, M' are at 270° C. The water tube system *Sc* surrounding the vacuum is shown; its action was explained in the former paper; the triple inlet *IW* and outlet *OW* are shown in Fig. 2. The funnel *Fu* which guards the window of the vacuum tube from heat given off by the large masses M, M' is also thoroughly protected from heating, by lagging, water tubes, and copper sheath. In order to prevent passage of air into the funnel its mouth is covered by a card with a rectangular hole *V* through which the two mirrors can be seen from the telescope. The funnel is supported on the table *Ta* which for stability is loaded at *Z*; and the vacuum sheath rests on a brass tripod *Tr* which stands on the cement slabs *C*.

The Outer System.—The large masses M, M, of lead, each of 47 kg, are carried with their heating coils *H* by rods and adjustable turn-screws *Y* attached to a girder beam *B* (3″ × 3″). This beam rests in a stirrup *St* and is supported from the wheel *R* which travels along the girder *G* (3″ × 6″). *G* stretches across the vault and its ends rest in recesses in the side walls and are there bricked in solidly. These girders and other supports are designed to carry a load of 300 kg; and in order that the rotation at *Th* and the to and fro movement of *R* on the girder *G* may be easy and smooth throughout an experiment, the former is provided with a thrust ball-bearing *Th* and the latter with a journal ball-bearing surrounding its axle. The wheel *R* can be brought to any desired position on *G* and rigidly clamped there by girder clips Q_1, Q_2, one on each side of *R*. Suppose that the rotating center *Th* has been brought accurately over the torsion head in the vacuum tube; then the masses M, M can be swung on *B* coaxially round the inner masses m, m, until the *A*, *B* positions of maximum couple are attained (see Fig. 3). Stops *S* are provided on a bracket *X* which is fixed on the end wall of the vault, and extension bars shown on the beam *B* are brought to these stops and are clamped there.

This system has mobility. It is possible during an experiment to unclamp either Q_1 or Q_2, rotate the beam *B* and run wheel *R* and all depending from it to one end of girder *G*, and then bring up an alternative system R' into position over the vacuum tube.

For further elucidation of the apparatus two photographs are given. Fig. 3, Front view as seen from one side of the telescope; Fig. 4, Back view, the telescope and scale being at the far end of the vault. The angle girders which carry the inner vacuum systems are seen prominently high up, Fig. 3. The Gaede pump and manometer, as also water pipes passing to and from the sink, are seen in both photos. In order to obtain clearer views, some outer wrappings have been removed from the

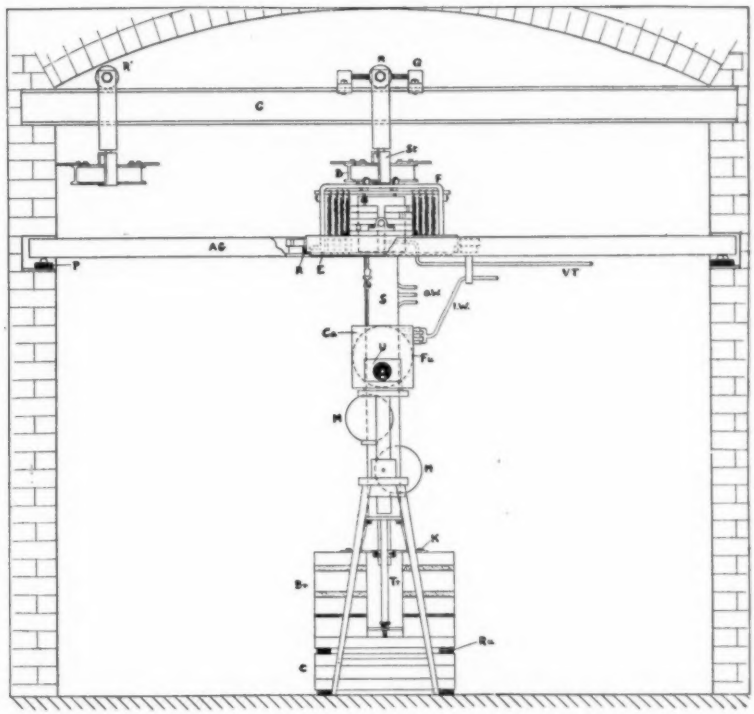

Fig. 2.

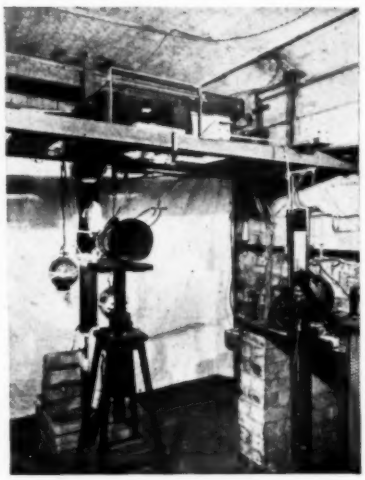

Fig. 3

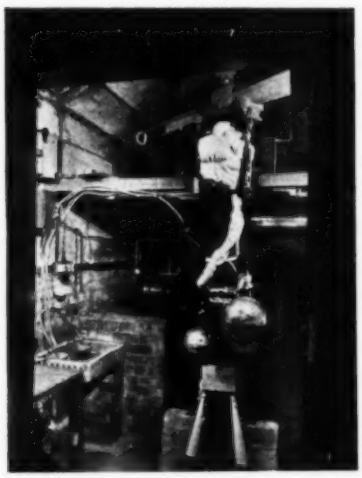

Fig. 4

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funnel and its supporting table. The two white surfaces seen so prominently in Fig. 4 are cotton wool lagging introduced for protection, respectively, of the top of the vacuum tube and of an exposed water pipe which passes round the sheath of the inner system. The scale used for the telescopic readings is 6 meters from the inner system. It is seen between the two bright horizontal surfaces at the far end of the vault, with the telescope field lens showing bright below it. The height and width of the room, as seen in Fig. 2 are each 10 ft.

To the right of, and 6 meters from the torsion balance, but not seen in Fig. 1, are the telescope and the scale graduated in mm. As explained in the former paper it is desirable to have two mirrors; one fixed to the outside of the vacuum tube, another in the usual way on the beam of the torsion balance. The former enables us to make correction for rotation, if any occur, of the vacuum tube. By deducting any rotation of the former mirror from that of the latter we obtain the true net rotation of the torsion beam. In the present arrangement both mirrors reflect light from *the same* scale whereas formerly the two mirrors reflected light from different scales into the telescope. Thus in the present arrangement we eliminate one link in the optical arrangement and avoid any error due to possible displacement of the two scales relative to one another.

In Fig. 5 we have a plan showing the vacuum tube with beam and

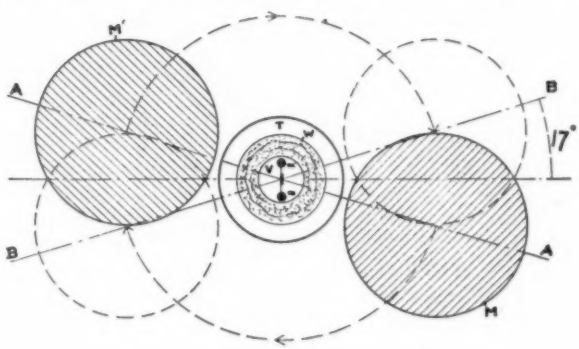

Fig. 5.

small masses m, m' surrounded by cotton wool W and the water tube space T. The large masses M, M' are shown set at the A position of maximum influence, 17° from the normal to the torsion beam. When the B position is required, the masses M, M' are swung round coaxially with V, as shown by the arrows. The shading of the masses is meant to show that M and m are in one horizontal plane whereas M' and m' are in another.

Experimental Results

The experiments were conducted and tabulated just as described in the old paper. The readings, in full, of one typical experiment are given in Table I. Columns 2 and 3 show the azimuth mirror readings of the vacuum tube and the beam respectively. In column 3 are shown the extreme scale readings as the beam swings to and fro. These are in sets of three, each set containing A and B positions alternately (see Fig. 5). The error of a single reading is generally only 0.1 mm but may be on occasions as much as 0.2 mm. Most of the latter error is due to the fact that the scale as seen in the telescope is generally quivering. In column 4 are entered the equilibrium positions Z, as found from column 3 by the expressions used in the previous research:

$$Z = C - \frac{(c-b)^2}{(a-b)+(c-b)} \qquad \text{or} \qquad Z = \frac{ad+b}{1+d},$$

where Z = equilibrium position; a, b, c are successive scale readings, and d = decrement. The results in brackets, column 4, are obtained from those immediately above by correcting for the tube readings, column 2. The last column gives the temperatures of the lead spheres M, M' as the experiment proceeds.

A glance at column 2 will show how steady is the reading of the tube azimuth, there being only 0.1 mm variation during the cold readings and 0.2 in the hot. In the old experiments this variation amounts to 0.5 mm or more. This rotation of the vacuum tube is as we have seen not in itself a source of error but it suggests that the vacuum tube has too great a degree of freedom relative to the large masses M, M'. And the movement of the outer system relative to the inner, brought about by heat, may have introduced errors in the results of the former experiment. This will be discussed further below.

Summarized results of the experiments are shown in Table II. In column 2 for dates 8/2 and 8/4 are shown two experiments C–H in which readings were taken with the coils in the lead spheres heated so that in those cases the temperature is rising during the experiment. It is more satisfactory to have temperature falling and no heating current passing, and this is the usual method; but it will be observed that the results for these two C–H experiments are not materially different from the other nine given in column 6.

To explain Table II., take as an example of cold and hot experiments those of date 7/30. For the first the temperature is 18°; for the second it falls from 230° to 140°. Seven results are found for the cold equilibrium position whose mean is 207.06 mm on the scale. Twelve results are found

for the hot with mean 206.98. The mean difference in range is − 0.08 mm. The minus sign indicates that the gravitative attraction between the masses is less when the masses M, M' are hot than when they are cold. In column 7 we see that the differences in equilibrium positions are not more than 0.3 mm cold and 0.3 mm hot. These are a measure of the accuracy with which scale readings can be taken in cold and hot experiments respectively, as the image of the scale moves to and fro in the field of the telescope.

TABLE I

A Typical Hot and Cold Experiment

Cold Readings					
1	2	3	4	5	6
Time	Tube readings mm	Torsion beam readings mm	Z Equilibrium position mm	Range mm	Temperature of M, M'
12.10 p.m.	208.5	280.5			18° C
		508.5	416.95		
		355.5			
				206.95	
		788.7?			
		513.4	623.9		
		698.0			
				207.0	
		277.1			
		510.8	416.9		
		353.8			
				207.2	
		788.4			
		513.9	624.1		
		698.0			
				207.2	
	208.6	252.3			
		527.6	417.0		
		342.9	(416.9)		
More water run in the tubes than this morning					
3.12 p.m.	208.6	253.5			18°
		527.1	417.2		
		343.4	(417.1)		
				207.0	
		792.1			
		511.7	624.2		
		699.5	(624.1)		
				207.0	
		265.0			
		519.1	417.2		
		349.1	(417.1)		
				207.0	
		510.4			
		701.1	624.2		
		572.3	(624.1)		
				207.06	MEAN

HOT READINGS

Same water flow as this afternoon

1	2	3	4	5	6
Time	Tube readings mm	Torsion beam readings mm	Z Equilibrium position mm	Range mm	Temperature of M, M'
8.25 p.m.	208.7	330.9			
		475.5	417.3		
		378.1	(417.1)		
	208.6	777.3			
		521.7	624.2	206.9	220°
		692.9	(624.1)		
8.40 p.m.	208.75	254.5?	417.2		
		526.2		207.1	213°
	208.8	344.2	417.3		
		466.5	(417.0)		
				206.95	200°
	208.7	749.1			
		540.0	624.1		
	208.6	680.7	(623.95)		
				207.15	194°
	208.8	264.5			
		519.5	417.1		
		348.4	(416.8)		
				206.9	188°
	208.7	781.8			
		518.1	623.9		
		694.8	(623.7)		
				206.85	180°
	208.8	266.3			
		518.6	417.25		
		349.2	(416.95)		
				206.85	172°
	208.7	517.5			
		695.4	623.9		
		575.9	(623.7)		
				206.9	165°
	208.8	291.0?			
		502.0	417.1		
		359.0	417.1		
		455.7	(416.8)		
				207.1	152°
	208.75	757.8?			
		534.3	624.1		
	208.7	684.5	(623.9)		
				207.1	147°
9.55 p.m.	208.8	263.7			
		520.0	417.1		
		348.0	(416.8)		
				206.95	140°
	208.75	775.6			
		522.5	624.0		
		692.1	(623.75)		
				206.98	MEAN

The oscillation period between consecutive readings, column 3, is 290 sec.

TABLE II

Summarized Results of Experiments

1	2	3	4	5	6	7	8
Date 1921	Nature of experiment C=cold H–C= from hot to cold	Temperature of large spheres MM'	Number of ranges taken	Mean range mm	Difference in mean ranges hot–cold mm	Extreme variation in equilibrium position mm	Extreme variation in tube readings mm
7/21	C	18°	12	208.43		.2	.45
7/22	C	18°	12	208.40	−.04	.2	.4
7/23	H–C	200°–130°	11	208.37	−.07	.4	.4
7/24	C	17°	7	208.46		.3	.4
7/25	H–C	210°–120°	11	208.38	−.07	.6	.2
7/26	H–C	240°–160°	8	208.40		.6	.2
7/30	C	18°	7	207.06		.3	
	H–C	230°–140°	12	206.98	−.08	.3	.2
8/1	C	18°.5	6	207.09		.3	
	H–C	250°–150°	12	207.08	−.01	.2	.0
8/2	C	18°	11	207.19		.4	
					−.10	.25	.1
	C–H	75°–160°	12	207.09		.6	
8/4	C	20°	7	207.11	−.08	.3	
	C–H	20°–220°	8	207.03		.3	.15
	H–C	230°–130°	13	207.19	+.09	.5	
8/6	C	19°	6	207.38		.3	.0
	H–C	215°–120°	10	207.40	+.02	.4	
8/7	C	19°	6	207.72		.1	
	H–C	220°–130°	11	207.60	−.12	.4	.2
8/10	H–C	230°–120°	7	207.53		.4	
	C	19°	6	207.63	−.10	.3	.15
				Mean	−.05		

Notes: (1) The vacuum for the first six dates was 10 mm. It was let down to 20 mm on date 7/30, and further to 25 mm on date 8/7. Apparently any vacuum between these limits is suitable.

(2) The water flows through the rubber tubes round the vacuum at the rate of about 1 litre per minute. The flow must be commenced at least two hours before the commencement of an experiment and is maintained constant until the experiment is over. The temperature of the water flow will then remain constant to 0.1°.

Now consider Table II. as a whole. The last column in Table II. shows that except in the first few experiments the scale, telescope, and vacuum tube are very nearly at rest relative to one another, since the extreme variation is not much greater than the smallest perceptible movement, 0.1 mm. Number 6 is the most important column as it shows the magnitude of the temperature effect, if any exist. These eleven results have values of 0.12 mm or less. Two have positive values, nine have negative, the algebraical mean result of all eleven experiments being − .05 mm. The temperature ranges are not the same in all the

experiments but this need not be considered in taking the final mean. The result − .05 mm seems to be an indication of a small temperature effect.

Taking the figures of this experiment we find that the probable error of the cold experiment is ± .03 mm and that of the hot experiment ± .02 mm, and the probable error of the mean of the whole series of experiments is less than .01 mm of scale.

TABLE III

Observed differences in ranges, hot minus cold, in mm.
Old series: + .58, .51, .48, .45, .42, .40, .38, .36, .32, .30, .28, .26; mean + .40.
New series: − .12, .10, .10, .08, .08, .07, .07, .04, .01, + .02, .09; mean −.05.

For comparison, the old and the new series of results for difference in range, hot–cold, are given in Table III. This shows clearly that the new results are more consistent than the old; and that the temperature coefficient, instead of being 1.2×10^{-5}, as given by the previous work, is certainly less than 2×10^{-6} and, in view of the observational errors, may well be zero.

It can be readily calculated that a small displacement of M, M' relative to m, m' of only 1 mm in a horizontal direction perpendicular to the line between them, or of 4 mm in a vertical or radial direction, if reversible with temperature, might give rise to an apparent gravitative temperature effect of the amount found in the earlier experiments. The old apparatus was carried by a stout wooden scaffolding firmly secured to the cement floor and vaulted roof and was crossed-braced with stout scantling. The scaffolding surrounded the apparatus, and though cards were used to screen heat from all wooden parts, the latter probably yielded during the heat experiments.

The apparatus has now been left intact as recently used; so that the work can be extended at any future time. Small modifications in it might be applied with advantage, chiefly with the view of confining the freedom of the outer and inner systems each to one degree, viz., rotation on a vertical axis. A serious difficulty which will be encountered in any attempt to attain a higher order of accuracy is the vibration of the torsion system. As this cannot be overcome by providing more freedom to its semi-floating supports and as the vacuum cannot be let down so as to damp out vibrations as they arise, there only remains the (unpleasant) course of conducting all standard experiments in the least vibrational period of the day, *i.e.*, between midnight and 4 a.m. One of us has already burnt much after-midnight oil on this arduous work. The removal of the apparatus to some spot in the country remote from

town vibrations is a luxury denied to those whose research must be done, if at all, in the town in which they work and in the College in which there exists suitable equipment, including work-shops.

These experiments and those published in 1915 are the only attempts to conduct the Cavendish gravitation experiment with hot bodies. They have shown conclusively that such gravitation experiments can be performed with high accuracy provided the torsion balance is in a vacuum and is surrounded by a protective screen of flowing water and non-conducting material. Contrasting the methods of the recent experiments with those of seven years ago, we see that there is no difference in the heating or the heat-screening arrangement or in the vacuum or its contents. This proves that the old effect which now appears spurious was not caused by heat trouble but probably by mechanical defects which we have now removed, and that our heating arrangements have all along been satisfactory.

We wish to record our great obligation to the Royal Society for a grant in aid of the research.

UNIVERSITY COLLEGE,
NOTTINGHAM, ENGLAND,
November 10, 1922

OVERTONES OF LARGE TUNING FORKS

By S. Herbert Anderson

Abstract

Overtones of large tuning forks.—*Elimination of the first overtone*, frequency 6.27 times the fundamental, which is usually very prominent for forks of pitch below 256 d.v./sec., can be secured by striking the fork with a soft, padded hammer at the internal node, situated one fifth the length of the prong from the free end, and at the same time holding the fork lightly at the antinode, situated two fifths the length of the prong from the fixed end. The elimination of this overtone has made it possible to detect a *new overtone* whose frequency is approximately three times that of the fundamental. This tone seems to be due to the vibration of the fork as an unsymmetrical free-free bar with one internal node 0.37 the length of the prong from the outer end and antinodes at the tips of the prongs and the tip of the stem.

IT has long been recognized that tuning forks are the most satisfactory sources of pure tones. As shown in treatises on Acoustics, the nodes of vibration of a tuning fork closely approximate to those of a fixed-free bar, in which the first three overtones have frequencies 6.27, 17.55, and 34.39, respectively, times that of the fundamental. When the forks are mounted on resonators tuned to the prime, the overtones are not generally noticeable, due to the fact that their intensity is small and the resonators do not have modes of vibration corresponding to these inharmonic overtones. While this is true for forks of pitch C_3 (256 d.v./sec.) and higher, the writer has found that in lower pitched forks the first overtone is very troublesome.

The prominence of the first overtone in large forks seems to be due to two causes: first, the prongs are relatively more slender than in higher pitched forks so that the stiffness is not as great and higher modes of vibration are favored; second, the long boards of the large resonator boxes are more readily forced into vibrating with the frequency of the overtones than is the case with the smaller resonators. It may be noted, in passing, that for this reason brass resonators of the Helmholtz or Koenig type are more satisfactory for large forks than the wood resonator boxes.

The prominence of the first overtone (which is the only troublesome one) may be somewhat reduced by using a soft, padded hammer and taking care to strike the prong only at the node for this mode of vibration, which is situated about one fifth the length of the prong from the outer end. But these precautions are not sufficient.

Some little time ago it was observed that if the prongs of the fork are grasped gently with the thumb and index finger at the antinodal point for this overtone, about three fifths the length of the prongs from the outer end, the first overtone can be effectually eliminated. The intensity of the prime is slightly decreased but not seriously, and this is more than compensated for by the purity of tone that is thus secured.

The elimination of the first overtone has made it possible to detect another overtone which apparently has not been noticed before. My attention was first called to this by Mr. Paul M. Higgs of this department when the above method of securing a pure tone was being demonstrated. This new overtone was found in all the large prong forks available in this laboratory. With C_1 and the G_2 forks, the pitch of the overtone is approximately an octave and a fifth above the prime; with the C_2 forks it is approximately an octave and a third. It could be heard in a C_3 fork, but is of too short duration to determine the exact pitch.

The accompanying table gives various data regarding the forks studied. The position of the node was found by running the index finger and thumb along the prongs as the fork was struck with a rubber hammer. Repeated trials showed the accuracy of this method very nearly as good as the one used for finding the node of the first overtone (described below). When the prongs are held at this nodal point and the fork is struck just a little above the yoke, the new overtone is brought out the loudest and all other tones are practically nil. The vibration seems to be a transverse vibration of the fork as a whole, extending from the node down through the yoke and stem. It may therefore be called the *stem* overtone. Loading the yoke lowered the pitch. The tips of the prongs probably have their velocities in the same sense instead of opposite senses as is the case with the prime, the mode of vibration being that of an unsymmetrical free-free bar with one node. This overtone is more prominent when the fork is mounted on a wood resonator box, provided the direction of vibration is parallel to the *width* of the box and not the length.

The frequency of the new overtone in each fork was found by counting the beats it produced with another fork of known frequency, except for the first two forks, for which forks of the required frequencies were not available. The duration of this overtone varied from about two seconds for fork number six to about five seconds for number one.

The position of the node of the first overtone was found by mounting the forks so that the flat faces of the prongs were horizontal, scattering a little chalk dust on the upper faces of the prongs, and bowing at the ends of the prongs while the prongs were damped at about one fifth the length of the prongs from the outer ends. The chalk dust gathered in a little ridge at the node. The frequency was found as for the new overtone.

TABLE I

Linear dimensions are expressed in centimeters; frequencies in double vibrations per second

Prime frequency f	Prongs				New Overtone			First Overtone		
	Lgth.[1] cm	Width cm	Thickness cm	Distance apart cm	Node[2]	Frequency f_s	f_s/f	Node[2]	Frequency f_1	f_1/f
64[4]	30.8	1.70	0.80	2.9	0.364	194[3]	3.03[3]	0.229	406.3	6.35
64[4]	29.9	1.88	0.90	4.9	0.378	183[3]	2.86[3]	0.268	399.0	6.23
128[5]	23.8	1.70	1.02	3.84	0.399	320.5	2.50	0.282	792.0	6.19
128[6]	21.3	1.94	0.80	3.34	0.376	309.7	2.42	0.237	800.0	6.25
128[4]	19.4	1.27	1.63	2.30	0.361	314.8	2.46	0.229	798.8	6.24
192[5]	18.0	1.49	0.89	1.85	0.345	517.0	3.16	0.238	1190[3]	6.2

By comparing the data for the two overtones, it will be observed that there is little greater uniformity in the position of the node in different forks for the stem overtone than for the first, but in spite of this there is less uniformity in frequency for the stem overtone than for the first. This is probably due to the fact that there is considerable variation in the shape and weight of the yoke and stem with different forks, and since the yoke vibrates as a whole, this will affect the frequency more in the mode of vibration of the stem overtone than in that of the first overtone.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF WASHINGTON,
SEATTLE, WASHINGTON,
January 6, 1923

[1] The length of the prong is the distance from the tip to the beginning of the curve of the yoke.

[2] The position of the node is given as the ratio of the distance of the node from the free end to the length.

[3] Approximately only.

[4] Maker Valentine and Carr.

[5] Maker Kohl.

[6] Maker Standard Scientific Co.

THE DYNAMICAL THEORY OF THE BRIDGE OF A CERTAIN CLASS OF STRINGED INSTRUMENTS

By K. C. Kar

Abstract

Vibration of a string; effect of letting it strike a sharp edge near one end, as in the case of the Indian plucked instrument tanpura, is to increase the relative intensity of the octave and other even harmonics while the rest diminish quickly almost to nothing, giving a peculiar sweet note. The *mathematical theory* is developed. The phenomenon apparently violates the Young-Helmholtz law since it may be observed even when the string is plucked in the middle; but the effect of the sharp edge is to build up the even harmonics even if they are very weak in the original vibration.

Introduction

STRINGED instruments may broadly be divided into three classes having three different modes of excitation, *e.g.*, (*a*) bowed, (*b*) struck, and (*c*) plucked. Dr. Raman has shown[1] that the musical instrument "tanpura" belonging to class (*c*) gives out a peculiarly sweet note when plucked at a point. He has suggested that this is due to some kind of periodic impact between the bridge and the string.

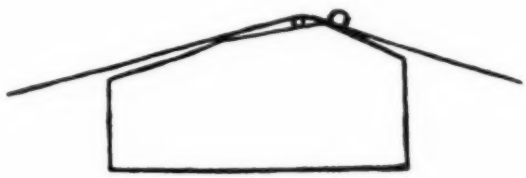

Fig. 1

This instrument, largely used in India, has no frets and is intended to be used as a drone accompanying vocal music. It has four metal "strings" which are stretched over a large resonant body and can be accurately tuned up to the right pitch by a simple device of continuous adjustment of tension. The special form of the bridge fixed to the resonant body over which the strings pass is indicated diagrammatically in Fig. 1.

In the present paper it is proposed to give the mathematical theory of the above phenomenon and some observations confirming the theory.

[1] Raman, Proceedings of the Indian Association, Vol. 7, 1921.

Observations

It has been observed by the writer that if any hard substance, *e.g.*, a finger nail, is brought near a stretched string at one of its ends, from above or below so as to touch it slightly in its zero position and the string is plucked at *any* point, it gives out a note exactly similar to that of the "tanpura." The nearer the nail is to the end, the finer is the adjustment required to produce the note. Thus it is possible by the above method to produce the same peculiar note in all stringed instruments. Now the effect of bringing the nail to the above position is to give periodic impact to the vibrating string at its zero position. Now the string passes twice in one period through its zero position. Therefore the impact occurs twice in every period. Thus the function of the bridge in the above instrument is to impart intermittent impulses to the string of a period equal to that of the octave.

The important characteristic of the note considered above is that soon after the note is produced the octave jumps into prominence while the intensity of the fundamental diminishes almost to nothing. The intensities of the other even and odd harmonics seem to increase and decrease respectively with time. The author hopes to give an account of his experimental work on the behavior of the higher harmonics on some other occasion. If, however, the impacts are not sufficiently strong, it takes some time before the rearrangement of the intensities of the different harmonics takes place.

Mathematical Theory

Thus the theory of the tanpura reduces to the case of vibration of a string under intermittent impulses with the periodicity of the octave. The solution of this problem will now be obtained by a very simple method discussed by the present writer in a recent paper.[1]

The equation of motion of a string in normal coördinates taking into account the damping [2] is

$$\ddot{\phi}_s + 2b_s\dot{\phi}_s + q_s^2\,\phi_s = \frac{2}{l\rho}\,\Phi_s.$$

The solution of the equation when $\Phi_s = 0$ is

$$\phi_s = e^{-b_s t}\left\{(\dot{\phi}_s)_0\frac{\sin p_s t}{p_s} + (\phi_s)_0\left(\cos p_s t + \frac{b_s}{p_s}\sin p_s t\right)\right\}.^{3}$$

If Φ_s acts at $t = t'$ for an infinitely small interval of time dt', ϕ_s at time

[1] K. C. Kar, Phys. Zeit. **24**, 63, 1923.
[2] Rayleigh, Theory of Sound, 2d Ed., Vol. I., p. 187.
[3] Ibid., p. 74.

t is given by

$$\phi_s = \frac{2}{\rho l p_s} \cdot \Phi_s dt' e^{-b_s(t-t')} \sin p_s(t-t')$$
$$= \frac{2}{l} \cdot \frac{u_s}{p_s} e^{-b_s(t-t')} \sin p_s(t-t'),$$

where u_s is the velocity imparted to the string by the force Φ_s.

Now if the force Φ_s instead of acting continuously acts only intermittently, *i.e.*, at $t = 0, \tau, \cdots n\tau$, the value of ϕ_s at time $(n+e)\tau$, where e is < 1, is given by

$$\phi_s = \frac{2}{l}\frac{u_s}{p_s}\Big[e^{-b_s(n+e)\tau} \sin p_s(n+e)\tau + e^{-b_s(n-1+e)\tau} \sin p_s(n-1+e)\tau + \cdots + e^{-b_s\tau e} \sin p_s e\tau\Big]$$
$$= \frac{2}{l}\frac{u_s}{p_s} e^{-b_s T}\Big[e^{-b_s n\tau} \sin p_s(n+e)\tau + \cdots + \sin p_s T\Big],$$

where $e\tau = T$.

In the case we are specially interested in here, the period of the impulse is that of the octave, so $p_2\tau = 2\pi$. Therefore $p_s\tau = \pi s$.

Thus we have when n is great

$$\phi_s = \frac{2}{l}\frac{u_s}{p_s} e^{-b_s T} \sin p_s T\left[1 \mp e^{-b_s\tau} + e^{-2b_s\tau} \mp e^{-3b_s\tau} + \cdots\right]$$
$$= \frac{2}{l}\frac{u_s}{p_s} \frac{e^{-b_s T}}{1 \pm e^{-b_s\tau}} \sin p_s T \text{ according as } s \text{ is odd or even.}$$

If the impulse acts at $x = x_0$, $u_s = u \sin(s\pi x_0/l)$. Therefore the equation of the string under intermittent impulse becomes after a certain time

$$y = \sum_1^\infty \sin\frac{s\pi x}{l}\frac{2}{l p_s}\sin\frac{s\pi x_0}{l} u \frac{e^{-b_s T}\sin p_s T}{1 \pm e^{-b_s T}}.$$

It appears from the above equation that the amplitudes of the different harmonics depend on the factor $(1/1 \pm e^{-b_s\tau})$, and that when the b_s's are small it becomes nearly $\frac{1}{2}$ for the first, third, fifth, etc., harmonics but ∞ for the second, fourth, etc., harmonics. Thus the effect of the periodic impact is to increase the intensity of the even harmonics and to decrease the intensity of the rest. If, however, the b_s's are very small, we are not justified in neglecting the natural vibration. So in that case it will be possible to hear the odd harmonics for some time.

Young-Helmholtz's law.—If a string is plucked exactly at its mid-point, the octave is, according to the above law, entirely absent from the

resultant tone. But in the "tanpura" it is not generally possible to stop the octave even by plucking in the middle of the string. Now it follows from the theory discussed above that only those harmonics which were completely absent initially drop out from the final equation. Their slight presence in the initial state of vibration makes them appear in full strength as required by the above equation. Thus the theory discussed above gives a satisfactory explanation of the apparent violation of Young-Helmholtz's law observed by Dr. Raman.

SCOTTISH CHURCHES COLLEGE,
CALCUTTA, INDIA,
26th NOV., 1922

NOTE ON A DEPARTURE FROM FRESNEL'S LAWS OF REFLECTION

By Nalini Kanta Sur

Abstract

Reflection of light from the common surface of two media having the same refractive index for certain wave-lengths was studied, the media employed being, first, freshly split rock-salt or clean glass against a suitable mixture of carbon disulphide and benzene, and, second, glycerine against turpentine. The reflected light did not vanish completely at the point in the spectrum where the refractive indices were equal but possessed a definite intensity that was practically constant at different angles of incidence. This reflection can hardly be due to contamination of the surface but must be due to a genuine change of refractive index in the surface layer.

SOME very interesting phenomena have been described by Rayleigh [1] in his experiments on reflection from the surface of a glass plate immersed in a liquid medium of which the refractive index has been equalized with that of the plate for any particular color. A mixture of benzene and carbon disulphide is taken in a cubical glass vessel with plate glass sides, and the glass plate after being carefully cleansed first with hot chromic acid and then with very dilute hydrofluoric acid is supported in the liquid. White light from a slit illuminated by a powerful source is allowed to fall on the glass plate and after reflection reaches the slit of a direct-vision spectroscope. When the angle of incidence is moderate (about 45° to 60°), the reflected light analyzed by the spectroscope shows a more or less diffused dark band in the green, for which the refractive indices of the plate and the mixture of liquids have been equalized. There is total reflection for indigo and violet, *i.e.*, farther from the dark band towards the shorter wave-length side, and the reflection gradually increases from yellow towards the red. Very careful cleansing of the plate is necessary to observe the phenomena, otherwise surface films mar the appearance greatly.

As the angle of incidence becomes very oblique, the region of total reflection approaches the dark band, which appears darker than before and also becomes well defined. On the other side the reflection increases gradually as before and becomes strong in the yellow and red. On the side of the longer wave-lengths the reflection is never total. The dark band is never completely dark and the increased darkness of the band at oblique angles of incidence is due to contrast only.

That surface film is partly responsible for reflection of the color of equalized index is shown easily. Some doubt may be entertained about

[1] Rayleigh, Scientific papers **6**, p. 95.

the entire removal of grease, etc., from the surface of the plate. To avoid cleansing and so remove this doubt, the different parts of the arrangement other than the plate are adjusted in position and then a small plate of rock salt is split along its natural surface of cleavage. By trial a plate with a plane reflecting surface may be obtained and it should be immediately immersed in the mixture of carbon disulphide and benzene with the same refractive index as the rock-salt plate for some particular color. The same phenomena are observed as before, but the dark band appears more prominently at all angles of incidence, showing that surface films are to some extent but not wholly responsible for reflection of the color of equal index.

If two different liquids of nearly equal refractive indices but not miscible with each other, such as glycerine and turpentine are put in the glass vessel and light from a horizontal slit is reflected from the clean common surface, a dark band is observed in the region for which the indices are exactly equal; and quite similar phenomena are observed in the spectroscope, the changes being continuous from moderate angles to very oblique angles of incidence as described before.

Some careful visual observations showed that with the indices equalized for green, the intensities of yellow or orange colors after reflection from the glass or the rock-salt plate, were greater for angles in the neighborhood of grazing incidence than when the angles of incidence were decreased.

Similar observations were made for blue. In this case the intensity of the reflected blue image increased as the angles of incidence decreased. This is easily explained by the fact that at moderate angles of incidence blue was totally reflected, but at grazing angles of incidence the region of total reflection was confined to the green.

The dark band was never completely dark and no perceptible change of intensity could be detected at different angles of incidence though the band always appeared comparatively dark at grazing incidence when other colors on either side were allowed to enter the spectroscope. This suggests that there is no real change of intensity in the dark region and that the apparent change in intensity is due to contrast only.

That surface contamination alone cannot account for the phenomenon is shown by the amount of light reflected in the dark band and also by the experiments made with two liquids of the same refractive index and not miscible with each other. This genuine change of refractive index is in all probability due to capillary phenomena at the surface.

The experiments were carried out in the laboratory of the Indian Association for the Cultivation of Science, Calcutta, and the author begs to record his thanks to Dr. C. V. Raman for his interest in the work.

EWING CHRISTIAN COLLEGE,
ALLAHABAD, December 10, 1922

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE WASHINGTON MEETING, APRIL 20 AND 21, 1923

THE 120th regular meeting of the American Physical Society was held at the Bureau of Standards, Washington, D. C., on Friday and Saturday, April 20 and 21, 1923. There were morning and afternoon sessions on both days with an attendance of about three hundred. The presiding officer was Professor Charles E. Mendenhall, President of the Society.

On Friday evening a joint informal dinner of the American Physical Society and the Association of Scientific Apparatus Makers was held at the Ebbitt Hotel, which was attended by about a hundred and fifty persons.

A special meeting of the Council was held at 1 P.M. on Saturday at the Bureau of Standards, attended by thirteen members. At this meeting it was voted to recommend to the Society an amendment to the By-Laws to increase the dues.

A special business meeting of the American Physical Society was held on Saturday afternoon at 2 P.M. The Treasurer, Professor G. B. Pegram, reported on the financial relations of the Society with Science Abstracts. The cost of publication having increased since the present arrangement went into effect, it would be necessary to increase the subscription paid per member from two dollars to three dollars if the Society were to assume its proportionate share of the cost of publishing this journal. The subscriptions from the American Physical Society form a large part of the total subscription list and it was the recommendation of the Council that we should assume our full share of the cost of publishing Science Abstracts A. To cover the increased cost of Science Abstracts and to provide additional funds for the Physical Review, the Council recommended that Article I, Section I, of the By-Laws be amended to read:

The annual dues of fellows shall be twelve dollars and of members nine dollars, payable on the first of January. Upon motion this amendment was adopted by the Society without negative votes.

President Mendenhall stated that an appeal would be made to the

individual members to contribute to a fund to make up the deficit in the cost of publishing Science Abstracts for the year 1923, and that the Council committee on Science Abstracts would be continued to make further arrangements as to Science Abstracts, including the matter of representation of the American Physical Society on the management of Science Abstracts and the whole subject of the coöperation of scientific societies in the publication of scientific abstracts in English.

The regular meeting of the Council was held on Saturday evening at the Cosmos Club. The following elections were made: *to fellowship:* Thornton C. Fry; *to membership:* F. L. Abbott, Antonius de Graaff, A. L. M. Dingee, Parke B. Fraim, W. R. Pyle, Alexander D. Ross, William H. Sanders, Humphreys O. Siegmund, Vernon E. Whitman, H. L. Wills, Enos E. Witmer.

The regular scientific session consisted of seventy-two papers. Abstracts of these papers are given in the following pages. Papers Nos. 6, 10, 24, 25, 35, 46, 47, 56, and 65 were read by title.

HAROLD W. WEBB,
Secretary

ABSTRACTS OF PAPERS

1. Mechanical wave-motion models having properties similar to electric wave-filters. THOMAS B. BROWN, George Washington University.—Simple chains of springs and mass particles may be constructed which not only are interesting in themselves as wave-motion models, but also serve to illustrate mechanically many of the physical principles of the Campbell electric wave-filters, having equations of identical mathematical form. The principles of construction are in general the usual ones for mechanical analogs of alternating current phenomena. The special case of a familiar wave-motion model (a chain of identical pendulums linked by identical springs) is first considered in detail, and this is followed by briefer discussions of a sufficient number of other special cases to illustrate the general methods of constructing such models. The mathematical treatment employed is more elementary than that usually used in the electrical cases, although quite as rigorous. A series of curves show, not only the critical frequencies and attenuation, but also the variation of velocity with frequency; and it is pointed out that models of this kind also illustrate in a general way the phenomena of dispersion of light, the equations for suitably modified systems leading to Sellmeier's dispersion formulæ.

2. The flow of liquids through capillaries. N. ERNEST DORSEY, Washington, D. C. —From a study of Poiseuille's observations, in which approximately cylindrical capillaries of circular bore and square-cut ends connect two large reservoirs of liquid, it is found that, contrary to the commonly accepted belief: (1) For rates of discharge corresponding to values of Reynold's number R ($= \rho vd/\mu$), less than 10, the viscosity as computed by Poiseuille's simple law, using the overall pressure difference, is strictly independent of the rate of discharge. (2) For $10 < R < 800$, the apparent viscosity, computed as above, exceeds the true viscosity in the ratio of $1 + k(R - 10)r/l_e$ to one where l_e is the effective length pertaining to rates of discharge below $R = 10$, and k is a purely instrumental constant. Values found for k differ among themselves, but average close to 1/16. (3) Hence, the intercept upon the pt axis, of the prolongation of the pt vs. $1/t$ graph in the region where pt varies, is less than the value of pt correspond-

ing to very low rates of discharge; the ratio of the two values is an instrumental constant. (4) If the intercept value of pt is used for an absolute determination of viscosity, an effective tube length that is less than that appropriate to very low velocities must be used. (5) For very short tubes it appears that the locus of $(\mu_o - \mu)/\mu$ vs. R becomes concave towards the axis of R when R exceeds a certain value, indicating that then the terminal turbulence has not had time to die out during the passage of the liquid through the tube.

3. Coefficient of slip and momentum transfer in air, hydrogen, and helium. E. BLANKENSTEIN,[1] University of Chicago.—The coefficients of slip in air, hydrogen, and helium have been determined by the constant deflection method, using liquid air and a constant flow of the gas to avoid impurities. Values have been obtained for a highly polished silver oxide surface which agree within the limits of the experimental error with Maxwell's equation when the fraction of the molecules that leave a moving surface with the equilibrium velocity is assumed equal to unity. The interpretation in terms of molecular reflection has been checked by observing the direct momentum transfer as a function of the pressure at very low pressures. The results agree with the simple kinetic theory for very long free paths, when "specular" reflection of molecules is assumed to be absent.

4. Internal friction theory of shaft whirling. A. L. KIMBALL, JR., General Electric Research Laboratory.—It is shown on theoretical grounds that an internal friction action, due to progressive bending in a rotating shaft, may cause the shaft to whirl at any speed above the resonant or first critical speed. The equations of motion of the shaft are derived for an ideal case taking account of internal friction, and solutions are obtained giving the motion of the shaft in the final state. No assumption is made as to the cause of internal friction. It may be due to a molecular friction producing a damping action in the shaft itself, or to a friction at its surface due to a working of the shaft in rings or other parts of the rotor which may be shrunk on to the shaft. Substantiation of the theory was obtained from experiments with a model shaft so built up as to have a large capacity for internal friction. This theory is a contribution to an investigation on shaft whipping and whirling being carried on by Dr. B. L. Newkirk, of the General Electric Research Laboratory.

5. Physics of lubrication. I. The carrying power of an oil film. MAYO D. HERSEY, U. S. Bureau of Mines.—Experiments at the Massachusetts Institute of Technology made some time ago, are here reported in detail with curves showing the gradual decrease of film thickness under increasing loads and the increase of carrying power (maximum load for a given film thickness) with speed. Film thickness is specified by relative electrical resistance, this being a maximum when journal and bearing are concentric, and zero when they are in metallic contact. The theory of carrying power is then worked out by dimensional reasoning, showing that if we assume a constant pressure coefficient of viscosity, the carrying power at constant temperature should go up more rapidly than the speed, approaching infinity as the speed approaches a certain critical value. Beyond this critical speed, any further increase of load would thicken the film.

6. A low voltage, low wattage mercury lamp. E. L. HARRINGTON, University of Saskatchewan.—The article describes a mercury lamp of great intrinsic brilliancy, providing a small capillary-tube-like source well suited for spectroscopic, laboratory, and demonstration uses. In form it resembles somewhat an ordinary spectrum tube without the lower enlargement. It is filled somewhat above the capillary portion and exhausted. The lamp requires a D. C. voltage of 25 or more, and operates in series with a control resistance on from .5 to .8 ampere. The lamp is started by breaking the thread of mercury at the lower end of the short capillary portion by the application of a bunsen burner at that point. It is constructed of pyrex glass.

[1] Introduced by A. J. Dempster.

7. A fallacy in the use of the wheatstone bridge. F. WENNER and NYNA L. FORMAN, Bureau of Standards.—During recent years there has gradually come into more or less general use, especially with alternating test currents, a practice of connecting one of the detector (galvanometer or telephone) terminals of the bridge to earth or to a conducting shield. This often materially improves the definiteness or precision with which the bridge may be balanced and for this reason it has been considered to be an advantage. It is now shown how such an arrangement may introduce errors equal to or even greater than those which would result from the indefiniteness of the balance which otherwise might exist, and further that other effective arrangements for improving the precision of the balance are to a large extent free from this fault.

8. A high temperature high vacuum furnace and its applications. H. C. RENTSCHLER and J. W. MARDEN, Westinghouse Lamp Company Research Laboratory, Bloomfield, N. J.—The furnace is of the high frequency induction type, with the coil and material to be heated placed close together in the vacuum container. The method of operation and the advantages of this arrangement are discussed in detail. With this furnace many rare metals such as uranium, thorium, zirconium and titanium have been produced in solid coherent form. X-ray tubes have been constructed with uranium and thorium targets produced in this furnace. A discussion is given of the use of the furnace for getting spectra of high melting metals, particularly in the deep Schumann region, for studying high temperature, high vacuum, chemical reactions, and for melting point determinations of such metals as react readily with gases. Other uses suggested are in the direct measurement of ionizing potentials of vapors of high melting metals and in the study of the isotopes of such metals.

9. The thermal conductivity of liquids under pressure. P. W. BRIDGMAN, Harvard University.—The thermal conductivity of some fifteen liquids has been measured up to a pressure of 12,000 kg/cm² at 30° and 75°. Most of these liquids are the same as those whose compressibility and thermal expansion have been previously measured over the same range (P. W. Bridgman, Proc. Amer. Acad. **49**, 1–114, 1913). The behavior of the thermal conductivity of all these liquids is roughly the same in character, increasing by a factor of two or three up to the maximum pressure. The temperature coefficient of conductivity, which is negative for all the liquids measured, decreases markedly at high pressures. The relation between conductivity and pressure departs greatly from linearity, the increase becoming less rapid at high pressures. Approximately, the increase of thermal conductivity runs parallel with the increase in velocity of sound.

10. Convection of heat by liquids. ROY A. NELSON, University of Illinois.—Convection currents in a liquid are traced by the shadows produced when a beam of light is passed through the liquid parallel to the axis of an electrically heated wire. Photographs of stream lines have been taken with heat losses as low as one calorie per centimeter per second. Liquids having different densities and viscosities have been used. For liquids of small viscosity, the photographs show that the heated column of the liquid above the wire is comparatively narrow, and motions may be studied as if in one dimension. For liquids of greater viscosity, the motion is more complex and stream lines can be seen at considerable distances from the side of the wire. The size of the image of the wire is changed when the wire is heated. This may be caused by a stationary layer of conducting liquid surrounding the wire. The rate of loss of heat from a wire can be expressed by the equation $h = a\theta^n$. Determinations of n for water, alcohol and carbon-tetrachloride give values of 1.15, 1.11 and 1.12, respectively. The value of a varies with the liquid. This work and calculations made from measurements of A. H. Davis (Phil. Mag. Nov. 1922) indicate that n for all liquids is approximately 1.15.

11. An intercomparison of the high temperature scales in use in this country with those in use in England. W. E. FORSYTHE, Nela Research Laboratories.—Several years ago the high temperature scales in use in several laboratories in this country were intercompared by measurements on several tungsten filaments sent out from this labora-

tory. The results obtained, as presented before this Society in 1917 (Phys. Rev., 11, p. 139, 1918), showed a very good agreement. Since that time the intercomparison has been extended to include the National Physical Laboratory of London through the courtesy of Sir J. E. Peteval. Dr. Stratton of the Bureau of Standards also kindly agreed to have measurements made on the same lamps. The tests on two lamps covered a temperature range from 1400 to 2750° K. The difference among the three laboratories was found to be only a few degrees at any point, varying from about an average of 2° from 1400 to 1800° K to about 5° at 2750° K. It is gratifying to note that the high temperature scales in use in England and in the United States are in such excellent agreement.

12. On temperature changes due to the expansion of gases at high pressure. H. E. REILLEY,[1] McGill University.—If a cubic foot of oxygen at 150 atmospheres pressure is allowed to expand rapidly into the atmosphere, the cylinder which contained it is cooled. This is Gay-Lussac's experiment. If thermocouples are affixed along the outside of the steel cylinder, it is found that the fall of temperature is greater near the bottom than near the top. If a cylinder at 150 atmospheres pressure is connected with a similar cylinder at one atmosphere pressure, and the oxygen allowed to pass rapidly from one to the other, the first cylinder is cooled and the second cylinder is heated. This is similar to Joule's experiment. By placing thermocouples outside both cylinders it was found that the fall of temperature of the first cylinder was about fifty per cent larger than the rise of temperature of the cylinder in which the gas was compressed. Similar experiments were made with hydrogen; but in this case the heating was slightly in excess of the cooling. These two experiments demonstrate the famous Joule-Thomson effects. If a cone provided with thermocouples is placed at the orifice of a high pressure cylinder, it is found that the thermocouple near the orifice is cooled more than that at the larger open end of the cone.

13. Physical properties of molybdenum, tantalum, nickel, and platinum at incandescent temperatures. A. G. WORTHING, Nela Research Laboratories.—Wires of the metals studied were rolled into ribbons, drilled with small holes at convenient intervals, wound on mandrils to form long closed tubes, and mounted on appropriate leads in ordinary lamp bulbs. With the tubes heated to incandescence, brightness measurements of the characteristic surface radiations and of the black body radiations from the holes were made with a disappearing filament pyrometer. These data served for the determination of the true temperature scales. The properties studied include spectral emissivity, total emissivity, resistivity, thermal expansion, and melting point. Spectral emissivity values have been extended to room temperatures by means of reflectivity measurements.

14. The drop electrode in molten salt electrolyte. PAUL B. TAYLOR, Bureau of Standards.—The drop electrode of Paschen has been studied in molten salt electrolyte. The cell Hg (still)|$NaNO_3$, KNO_3, $LiNO_3$, ternary eutectic|Hg (fine stream) has an e.m.f. of .66 ± .02 volt, still electrode positive. There is no temperature coefficient between 138 and 220° C. The cell Hg (still)|$NaNO_3$, KNO_3, $LiNO_3$, ternary eutectic amalgam Hg .85, Bi .15 (fine stream) has an e.m.f. of .735 ± .002 volt, still electrode positive. There is no temperature coefficient between 158 and 172° C. The cell Hg (still)|$NaNO_3$, KNO_3, $LiNO_3$, ternary eutectic|amalgam Hg .85, Bi .15 (still) has between 162° and 238° an e.m.f. which may be represented by $E = .001110T \pm .004$ volt where T is the absolute temperature. The mercury electrode is positive. The results show that the e.m.f. of the dropping electrode is independent of the metal of the electrode. Thus while the difference in e.m.f. between pure mercury and the bismuth amalgam was .483 volt at 162° C, the difference between them as streams was only .07 volt. Higher velocities of flow might have reduced this difference still further.

15. The auditory masking of one pure tone by another and its relation to dynamics of the inner ear. R. L. WEGEL and C. E. LANE, A. T. and T. and Western Electric

[1] Introduced by A. S. Eve.

Research Laboratories.—Data are given on the masking of one pure tone by another as the intensity and frequency of each are varied. For tones introduced into the same ear, except when the frequencies are so close as to produce beats, the masking is greatest for tones nearly alike. When the masking tone is loud it masks tones of higher frequency better than those of frequency lower than itself. When the masking tone is weak there is little difference. Little masking occurs for tones introduced into opposite ears unless the masking tone is loud enough to be conducted through the head and produce direct stimulation of the opposite ear. The response of the ear appears to be a power series function of the sound pressure. The data, together with Knudsen's data on frequency sensibility, are interpreted in terms of the dynamical theory of the cochlea which ascribes its frequency selectivity to an attenuation of vibrations along its length and a shunting through narrow regions of the basilar membrane at points depending on the frequency. Conjectured curves are given for a few single frequencies, of the amplitude of vibration of this membrane as a function of the distance along it.

16. Velocity of sound by a phase indicating device. P. I. WOLD and E. B. STEPHENSON, Union College.—Sound from a single source of known frequency is passed through a divided path of two tubes, one fixed and one variable, to microphones, one at the end of each tube. The output of these microphones is amplified and impressed on the two pairs of plates of a Braun tube. On varying the length of one tube the Lissajous figure passes through its various phases and permits an accurate determination of the wave-length, and thus the velocity, of the sound. The method has been used to measure the velocity of sound in tubes as a function of the diameter and the frequency.

17. An extension of acoustic wave filter theory. G. W. STEWART, University of Iowa.—It was anticipated that if acoustic filters were used at frequencies whose wavelengths were comparable to the length of the acoustic conduit of one section, thus violating one of the assumptions of the original theory, the computations concerning attenuation would be incorrect and that, indeed, transmission would occur at frequencies where the simple theory would specify high attenuation. This is found to be the case with the low-frequency-pass and single band filters previously described. In both cases a series of bands are transmitted at higher frequencies. It is now found that if the conduit at these higher frequencies is assumed to possess both inertance and capacitance in series and if the values of these are obtained by assuming them the same as at resonant frequencies and if corresponding changes are made in the original theory, the number and frequency limits of these additional bands are determined with a satisfactory degree of approximation. Moreover, if the formulæ specify a very narrow band, experiment shows that it is practically nonexistent. Thus by correct design the cut-off region of a filter can be made very much more extensive than would at first seem possible.

18. New vibrations within a conical horn. VICTOR A. HOERSCH, University of Iowa.—The solution for simple harmonic vibrations within an infinite rigid cone was obtained in terms of Bessel and Legendre functions. The solution is dependent on two parameters, one the frequency, which may be arbitrary, and the other a parameter capable of having an infinite set of discrete values. This solution was applied to a finite horn in an approximate way by assuming that the velocity potential is zero over the opening of the horn. In this case, for each value of the second parameter, the frequency is capable of having only an infinite set of discrete values. For the second parameter zero, the frequencies obtained are those of the classical theory in which the vibrations of the medium are everywhere radial with respect to the vertex of the horn. Other values of the second parameter represent vibrations of a new type in which the vibrations of the medium have in general a transverse as well as a radial component.

19. What is the physical criterion which determines the pitch of a musical tone? H. FLETCHER, A. T. and T. and Western Electric Research Laboratories.—It has been generally understood that the pitch of a compound tone is determined by the frequency of the fundamental. Experimental tests with electric wave filters connected into a high quality telephone circuit have shown that this is not necessarily true. The pitch

of vowels which are sung by a bass, a baritone, or a contralto is not changed when the fundamental and first few overtones are eliminated. The quality is modified but the pitch remains unchanged. The same is true of musical instruments of low pitch which are rich in harmonics. These results indicate that pitch is determined by the difference in frequency between the tones in the series of harmonics, especially in the louder ones, rather than by the frequency of the fundamental tone. In explanation it is suggested that since the transmission mechanism of the inner ear is non-linear in its response to an external force, subjective harmonic, summation, and difference tones are produced when the ear is stimulated by a compound tone; consequently, if the fundamental or first few harmonics of a musical tone, which is rich in harmonics, are eliminated from the external source, they are again introduced by the inner ear with sufficient magnitude to maintain the pitch at the same position on the musical scale.

20. Permalloy, an alloy of remarkable magnetic properties. H. D. ARNOLD and G. W. ELMEN, A. T. and T. and Western Electric Research Laboratories.—It is found that a wide range of nickel-iron alloys containing more than 30 per cent nickel are, when suitably heat-treated, more easily magnetizable in weak fields (less than 1 gauss) than any previously known material. The peak value of the initial permeability (permeability extrapolated to zero field) occurs near 78.5 per cent nickel and may be as high as 13,000 or more than 30 times that of the best soft iron. The name "permalloy" is chosen for these highly magnetic alloys. Methods of preparing and conditioning permalloy are outlined, and a representative chemical analysis is given. Measurements of permeability were made in a special permeameter suitable for highly permeable and sensitive materials. Permalloy is also characterized by very low hysteresis losses. The effects of mechanical stress upon permeability and upon electrical resistance, the effects of magnetization upon resistance and upon dimensions, and the joint effect of stress and magnetization upon resistance are all discussed qualitatively, the effects being large, easily produced and, within certain limits, completely reversible. The material is accordingly of great scientific interest. Its remarkable characteristics make permalloy of unique value in telephony and telegraphy, particularly in submarine cables.

21. Magnetostriction in iron and permalloy. L. W. MCKEEHAN and P. P. CIOFFI, A. T. and T. and Western Electric Research Laboratories.—The method used was based on one devised by Pupin (J. R. Hobbie, Jr., Phys. Rev. **19**, 456–466, 1922). A vertical wire or tape was magnetized simultaneously by an alternating field of constant amplitude ΔH, less than 0.01 gauss, and by a direct field H of any desired amount. The rapid changes in length of part of the sample produced torsional vibrations in a rochelle salt crystal, the alternating current output from which was amplified and measured, conditions of resonance being avoided. Calibration was effected by vibrating the crystal with a half-frequency alternating potential applied across an air-condenser. The sign of the magnetostriction was determined oscillographically. The most striking result was that the effect measured (differential magnetostriction) was zero when the direct field H_0 annulled that due to the earth's magnetism. Maxima in the effect occurred at $H_0 \pm H_m$; in pure annealed iron $2H_m$ was about one gauss; in a particular sample of permalloy, maxima nearly one hundred times as great were still closer together so that one maximum was actually attained in the uncompensated earth's field. Beyond the maxima the curves fell away to zero as saturation was approached. The work reported forms part of a study of the relations between magnetostriction, permeability, and electrical resistance.

22. Characteristics of iron in high frequency rotating magnetic fields. LEWI TONKS, Columbia University.—A method for obtaining a uniform magnetic field rotating at a high frequency has been devised. Measurements on the susceptibility and hysteresis in a thin disk of iron were made in fields of 0.5 to 5 gauss at frequencies varying from 52 to 168 kilocycles. Calculations were made allowing for incomplete penetration and the demagnetizing factor of the disk. When the intensity of magnetization was 350, the susceptibility of the iron decreased from 98 at 52 kilocycles to 74 at 168 kilocycles.

The angle of lag varies with frequency and shows a maximum between $I = 450$ and 600. Hysteresis energy loss per cycle for constant intensity of magnetization increases and for constant field decreases with increasing frequency, and follows, roughly, the law $E \propto I^{1.9}$ at all frequencies.

23. Cathode ray oscillograph: time-distribution of potential in a Geissler tube. DAVID A. KEYS, McGill University.—The present paper contains an account of some experiments on the measurements of the time required for the potential in a Geissler tube to reach its equilibrium distribution after the potential difference is applied to the electrodes. The method consists in having a movable sounding electrode placed between the two electrodes of the discharge tube. The exploring electrode, which is initially at the same potential as the cathode, takes up the potential of the surrounding gas. The time-potential curve is determined with a cathode ray oscillograph (see Glazebrook, Dictionary of Applied Physics, vol. 1, p. 76), the insulated plate of which is attached to the exploring electrode. The results confirm the work of Aston on the electric force in the dark space. The times of adjustment, in ten-thousandths of a second, varied from 1 to 80 in the case of air. It was found that the time varied inversely as the distance from the cathode throughout the Crookes dark space, and remained constant throughout the negative glow. This problem was suggested by Sir Joseph Thomson.

24. Determination of the mobility of the ions in the corona discharge. WM. M. YOUNG,[1] University of Illinois.—In order to test the theory of the corona pressure given by Jakob Kunz, the mobility of the ions in the corona discharge has been directly measured by blowing a current of air through the corona and afterwards through two successive cylindrical ionization chambers. The ionization current in the second chamber shows a well-pronounced maximum as a function of the potential difference. The mobility of the ions of air was found in the first measurement to lie between 3.7×10^{-3} and 1.2×10^{-3} cm per sec/volts per cm, agreeing well with the values deduced by Kunz from the pressure increase alone.

25. The current voltage relation in the corona. C. S. FAZEL and S. R. PARSONS, University of Michigan.—The best theoretical relation between voltage and current in the corona has been obtained by Townsend, but his equation expresses the voltage as an implicit function of the current. The equation may be simplified by assuming that the ratio of the current to the product of the mobility and the starting gradient is very small, and the approximation thus introduced may be improved by allowing the point at which the initial gradient is maintained to move out as a linear function of the potential. The resulting equation is of the form $i = A(V - V_0)V/(V_1 - V)$ where V_0 is the starting voltage and V_1 is a voltage of the nature of the arcing voltage, although it is not expected that the above equation will hold up to the arcing voltage.

26. The Hall effect and specific resistance of cathodically deposited films of gold. S. S. MACKEOWN, Cornell University.—The films used were seven centimeters square, and the thickness varied from 5 mμ to 80 mμ. The thickness was computed by weighing the mass of gold deposited on very thin mica. The usual density was assumed. The transmission of monochromatic light was measured and Beer's law was found to hold. This gave a convenient way of determining the thickness of the films used in measuring the Hall effect and specific resistance. The Hall constant was found to be the same as for gold in bulk, independent of the current, magnetic field strength, and thickness. It was not affected by heat treatment or ageing of the films. The specific resistance increased rapidly with decrease in thickness, being about fifteen times the normal value in the case of the thinnest films. The resistance could be varied greatly by heat treatment and ageing. These results support the theory that the high specific resistance of sputtered films is due to poor electrical contact between particles.

27. The electric capacity of cell suspensions. HUGO FRICKE, Cleveland Clinic.—In its electrical aspect a cell suspension is equivalent to an ohmic resistance combined

[1] Introduced by Jakob Kunz.

in parallel with a certain capacity; the value of this capacity, when the volume of the suspension is 1 cc, is called the capacity of the suspension. Assuming that a single cell can be regarded as consisting of a well conducting interior surrounded by a membrane of low conductivity, a formula has been derived giving the capacity per cm^2 of cell membrane as a function of the capacity of the suspension, the number of cells per cc, and constants defining the single cell geometrically. This formula has been verified by measurements by a bridge method of the capacity of the red corpuscles of rabbits. This capacity per cm^2 of membrane is .80 μF, the value being independent of the frequency (between 20,000 and 100,000 cycles) and of the composition of the intercellular liquids. In accordance with the hypothesis that the effect of the polarization at the membranes is negligible, the thickness of the cell membrane can be calculated to be 4×10^{-7} cm, using 4 as the value of the dielectric constant.

28. An experimental demonstration of the instability of a cylindrical liquid column. R. A. CASTLEMAN, JR., Bureau of Standards.—As is well known from the work of Plateau and Rayleigh, a cylindrical liquid column becomes unstable, under the influence of a vibration of frequency n, when its efflux velocity exceeds that given by $V_c = \pi n d$, where d is the diameter after contraction. In these experiments, the jet was shot horizontally from an orifice $\frac{1}{8}$ inch in diameter, in a thin brass plate. The head on the jet could be varied, or kept quite constant. The orifice chamber was influenced by an electrically driven 250-cycle fork. The process of disintegration was examined by (*a*) stroboscopic means, and (*b*) spark photography. As long as the efflux velocity is greater than the v_c, the process of disintegration is seen to be progressive. If, now, the head causing flow is decreased, a point is reached where the amplitude of the initial disturbance remains stationary, the disturbance itself, as seen stroboscopically, becoming harmonic. The efflux velocity at this point is found to conform closely to computed v_c if the linear contraction coefficient is taken as 0.8. Instability, of course, sets in when the velocity is increased by gravity to v_c. This phenomenon is readily shown stroboscopically, but on account of its erratic nature, photographic recording—by the spark, for instance—is difficult. However, some satisfactory spark pictures have been obtained.

29. Resistance measurements on bodies in a high-speed air-stream. L. J. BRIGGS and G. F. HULL, Bureau of Standards.—The air stream was obtained by allowing a continuous supply of compressed air from a powerful centrifugal compressor to expand through a cylindrical orifice 12 inches in diameter at the top of a vertical standpipe. The speed and temperature of the jet were computed from the speed, temperature, and pressure of the air in the standpipe, assuming an adiabatic expansion. Air-speeds up to the speed of sound have been employed in the resistance measurements, which have been conducted for the Ordnance Department, U.S.A., and include drag and cross-wind forces on models of projectiles and head-resistance measurements of bomb models, stream-line bodies, and spheres. For head-resistance measurements a piston type of balance was most satisfactory. The cylinder of the balance is supported from a stream-line bar, co-axial with the vertical air-stream. A spindle projecting downward from the piston is attached to the trailing end of the model. In measuring the force, the pressure in the cylinder is varied until the model is floating in the air-stream. Head resistance was computed from the weight of the moving system, diameter of the piston, and the differential pressure. A correction for the resistance of the spindle was made. Resistance measurements on bomb models have been made throughout the speed range of bombs during flight. The measurements were carried out at Lynn, Massachusetts, through the courtesy of the General Electric Company.

30. A diffraction phenomenon observed in night photographs. ENOS E. WITMER,[1] University of Pennsylvania.—It is frequently observed in night photographs that each light is the center of a figure consisting of an even number of luminous rays diverging

[1] Introduced by Arthur W. Goodspeed.

from it as a center. These are diffraction figures due to the polygonal form of the aperture of the interlens diaphragm. Experiments made by the author during the winter of 1920–21 demonstrate that in the case of a camera focussed on a luminous point source the diffraction pattern of an aperture can be determined by the following rule: Find the geometrical shadow of the aperture on the conjugate focal plane, assuming the lens or lenses are not present. Through the image of the luminous point on the conjugate focal plane draw straight lines perpendicular to the boundary of the geometrical shadow. This set of lines determines the directions of the luminous rays diverging from the image of the luminous point. It is interesting to compare this rule with the conclusions of Becknell and Coulson (Phys. Rev. **20**, pp. 594 and 607, 1922).

31. The fine analysis of the Stark effect in Balmer's series by Lo Surdo's method. JOHN STUART FOSTER, National Research Fellow, Yale University.—The essential feature of this investigation is a new form of Lo Surdo discharge tube, which is so constructed as to avoid the usual harmful effects of cathode pitting. The plates were taken with a large glass prism spectrograph, the mountings of which are of metal throughout. The method excludes any doubt regarding ghosts, and enables one to estimate relative intensities of components in the presence of the secondary spectrum. In addition, the effect is recorded for a large range of fields on one plate, and the light intensity is such as to permit the observations to be extended to H_ϵ. With increasing field strength no very marked changes in the relative intensities of components were noted. Among the p-components for H_γ, however, the undisplaced line grows weaker with increasing field and finally disappears. The outside s-components for H_γ are very weak in all fields up to the maximum value of 60 kv/cm and are about equal in intensity. Stark is doubtful regarding these latter components at 75 kv/cm, but records a great difference in the intensities. The new observations are in better agreement with Kramer's theory. The second order effect is shown on one plate for H_γ, H_δ, and H_ϵ. Thirteen components for H_ϵ have already appeared and there is reason to believe that more can be found. The new data, which includes some observations on the effect in helium, will be published in detail soon.

32. New series spectra in oxygen. J. J. HOPFIELD, University of California.—Three new series spectra have been discovered in the region 1000–1300 A determining a new triplet term Op_{123} in oxygen. The frequency numbers of the components of this triplet term as calculated by the combination principle from the observed triplets are 109833.8, 109673.4, and 109606.9 with an average deviation from the average of 1.2, 0.7 and 1.4 respectively for the eleven observed lines. (The twelfth is probably lost in the absorption band of oxygen.) Lines of these new series have been observed for the combinations $Op_{123} - 1S$, $Op_{123} - 2S$, $Op_{12} - 1s$ and $Op_{123} - 2D$, Op_1 indicating the level of highest frequency number. This new triple energy level is probably the valence level for oxygen and hence a p level, since it corresponds to the two 2_2 orbits on the new Bohr theory. This gives for the first time a triple valency level, and it is also the first known valence level for the sixth column of the periodic table. The corresponding highest resonance and ionizing potentials are 9.11 and 13.56 volts respectively. The results seemingly indicate three slightly different ionizing and resonance potentials corresponding to different stable forms of the atom. A few other lines of oxygen are also found in this region. They are now being studied.

33. Quantum defect and the new Bohr theory of atomic structure. F. S. BRACKETT and R. T. BIRGE, University of California.—Relations between quantum defect and the number of orbital groups of electrons in the atom, as proposed by Bohr, are shown and these form the basis for the assignment of quantum numbers to the orbits, giving rise to the known series spectra. This assignment is in agreement with that proposed by Bohr for the singlet and doublet spectra, with the exception of the orbits of azimuthal quantum number three. In this case it is not found necessary to assume the existence of orbits of the same quantum number inside and outside the atom body. The assignment of levels associated with the triplet spectra leads to the conclusion that the oxy-

gen-sulphur-selenium group and the zinc-cadmium-mercury group are homologous to the alkaline earths in regard to quantum defect. For orbits of azimuthal quantum number one and two, the quantum defect is strictly proportional to the number of orbital groups of electrons in the atom body for ranges where groups consisting of four electrons are added to the atom body. The successive initial development of the quantum defect in the circular orbits 2_2, 3_3, 4_4, 5_5, and 6_6, is made the basis for the estimation of the extent of the atom body. The denominators for the orbits of higher quantum number are obtained from the assignment of levels giving rise to lines in the infra-red for the heavier alkali metals.

34. Isotopes: a new relation concerning atomic species of even and of odd atomic weight. WILLIAM D. HARKINS, University of Chicago.—In general there are only one or two isotopes of elements of odd atomic numbers, and these have odd atomic weights. Above atomic number 28 the number of isotopes of elements of even atomic number is considerably larger, and commonly from five to about nine. As a general rule, and especially in the case of the more abundant atomic species, the atomic weights are even if the atomic number is even. However, there is a much smaller number of less abundant isotopes of even atomic number but odd atomic weight. The present relation concerns the existence of this last type. It is found that, at least up to atomic number 36, such isotopes occur in an even numbered element only when in the adjacent elements of next higher and lower (odd) atomic number there are isotopes of the same isotopic number. Thus there is an evident connection between the atomic species of odd atomic weight, whether the atomic numbers are odd or even. In the region of atomic number 50, isotopes of this type occur when in one adjacent (odd) element there is an isotope of the same isotopic number. Thus the atomic species of odd atomic weight form a different type of system from those of even atomic weight.

35. Relativity, quantum theory, and the wave theories of light and gravitation. A. C. LUNN, University of Chicago.—This paper is a preliminary report on a theory originally sought in order to meet the recognized need for a reconciliation between wave theory and quantum phenomena; its scope of adaptation proves to be quite wide. It includes (1) a wave theory of gravitation in quantitative connection with optical, electronic, and radioactivity data; (2) a related general suggestion of a theory connecting molecular properties with properties of matter in bulk; (3) alternatives for some of the current features in the theories of atomic structure; (4) a new interpretation and deduction of formulas for series and band spectra, using in lieu of the quantum condition a substitute directly related to long familiar physical notions; (5) a modification of Lagrangian dynamics which promises to be of service in the study of complex atomic and molecular structures; (6) a non-quantum theory of specific heat and black radiation. Results so far reached deal mostly with problems approachable by elementary methods or approximate computations. A set of formulas has been obtained which yield computation of the electron constants e, h, m, and mass-ratios, assuming from observation only the Rydberg constant, velocity of light, gravitation constant, and Faraday constant, with results in each case in practical agreement with measured values.

36. The line and band spectra of fluorine. HENRY G. GALE, University of Chicago.—The spectrum of fluorine, generated by the electrolysis of KHF_2, has been examined in vacuum tubes provided with fluorite windows. The spectrum is very bright at pressures of about 3 mm of mercury, and could be photographed in the first order of a 21 ft concave grating. The stronger lines, produced formerly by a spark between gold electrodes in an atmosphere of fluorine at atmospheric pressure, have been remeasured, together with a number of fainter lines apparently due also to fluorine. Five strong bands with heads at approximately 5100, 5390, 5730, 6100, and 6520 A, and six fainter bands with heads at approximately 5580, 5720, 5850, 6480, 6930, and 6980 A, have been photographed and the stronger lines measured. All these bands are degraded toward the red. These bands were found under a sufficient variety of conditions and with sufficiently elaborate experimental precaution so that it appears rather cer-

tain that the bands are due to fluorine and not to any compound. Attempts to secure the spectrum of HF yielded only the Balmer lines and the lines of the secondary spectrum of hydrogen. *Silicon tetrafluoride* gives a band spectrum of eleven bands between 4240 and 4600 A. These bands are degraded toward the red and appear to fall in three groups.

37. The 3883 CN band in the solar spectrum. RAYMOND T. BIRGE, University of California.—A critical study of the 3883 band in the solar spectrum has yielded a list of 188 lines, apparently not blended, and suitable for wave-length measurements. This study has been made with spectrograms from the Mt. Wilson Observatory, and with numerous enlargements. The lines have been weighted from 1 to 16,—very low to very high weight. The relative wave-lengths of these lines, in the arc and in the sun, have been measured on a plate of 2.5 mm per Angstrom dispersion, and are found to be the same within limits of error. (Average deviation 0.0003 A for 5 very high weight doublet pairs, 0.0012 A for 18 high weight, 0.0019 A for 37 medium weight, etc.) This indicates that any solar shift, if present, is common to all the lines of this band. Also, previous data on stable iron and CN lines in the Rowland and International system indicate in general a similar behavior in the solar spectrum. St. John's 42 line pairs, as now weighted, yield + 0.0014 A shift by his method (a), and + 0.001 A by method (b). Grebe and Bachem's 36 lines, similarly reweighted, yield + 0.0039 A shift. However, most of the seemingly best lines lie further to the violet than the region used by all previous investigators of the Einstein shift.

38. Computed and observed infra-red resonance frequencies in diatomic solids. E. F. NICHOLS and E. Q. ADAMS, Nela Research Laboratories.—On the basis of the simplest assumptions, an attempt is made to compute the resonance frequency of the single infra-red absorption band occurring in diatomic solids. Assuming Hooke's Law, resonance frequencies are computed, as follows: $\nu = (1/2\pi)\sqrt{(E/I)}$, $E = 4\pi e^2/\Delta(n^2)$, $I = m_1m_2/\delta$, in which m_1, m_2 are the masses of the two kinds of atoms, δ the density, e the electron charge (e.s.u.), and $\Delta(n^2)$ the total change in dielectric constant for the whole range of dispersion due to the resonance frequency in question, as it appears in the Ketteler-Helmholtz equation. The substances for which comparison is made are the fluorides of lithium and sodium; chlorides of sodium, potassium, and silver; bromides of potassium and silver; potassium iodide; and zinc sulfide (sphalerite). That the agreement of theory with observation is only approximate is probably due to the fact, that certain of the assumptions have been unwarrantably over-simplified. New experimental material is communicated which includes measurements of the *reflecting power for 6 mm electric waves*, of rock salt and fluorite and of fused mases of sodium and lithium fluorides, potassium and silver bromides, potassium iodide and silver chloride. New residual wave groups are reported for lithium and sodium fluorides and for boron nitride.

39. The structure of the absorption bands of certain organic gases and vapors in the near infra-red. CHARLES F. MEYER and DETLEV W. BRONK, University of Michigan.—A large number of organic compounds show a remarkable similarity in their spectra in the near infra-red, and particularly between 2 and 4 μ. This was brought out by the work of W. W. Coblentz and others, who examined the substances with low dispersion. Modern theoretical developments have suggested that with higher dispersion it might be possible to analyze these spectra so as to obtain quantitative relations which would throw some light on the molecular structure of the compounds. Many of the substances have prominent absorption bands in the regions 2.4, 3.3, and 7.0 μ. Thus far the region of 3.3 μ has been carefully investigated for ethylene, benzene, ethyl alcohol and ethyl ether. The bands exhibit decided structure, each yielding several absorption maxima. Ethylene (C_2H_4) shows prominent maxima at 3.1970, 3.2412, 3.3169, and 3.3722 μ, of approximately the same intensity. The group somewhat suggests a double doublet. Benzene (C_6H_6) shows three maxima at 3.2331, 3.2784, and 3.3722 μ. The central one at 3.2784 μ is by far the most pronounced.

Ethyl ether ($[C_2H_5]_2O$) has two very decided absorption maxima at 3.3513 and 3.4802 μ of about equal intensity, and a smaller maximum between the two at 3.3973 μ. Ethyl alcohol (C_2H_5OH) has one decided maximum at 3.3571 μ, and several less intense maxima; the most pronounced is at 3.45 μ. Examination of the absorption curves indicates relationships in wave-length differences between the maxima for the compounds.

40. The relative intensities of band components in the infra-red spectra of diatomic gases. E. C. KEMBLE, Harvard University.—*Calculations from the correspondence principle.* A diatomic molecule rotating with a frequency ω_r and vibrating with a frequency ω_0 would emit sensibly equal amounts of energy of frequencies $(\omega_0 + \omega_r)$ and $(\omega_0 - \omega_r)$ according to classical theory. It follows that the relative intensities of the lines in the absorption bands should be proportional to λ^3 and to the numbers of molecules in the corresponding initial states. The equality of the intensities of the components adjacent to the central gap in the HCl band at 3.5 μ shows that they come from the same initial state and that the initial rotational quantum number is not fractional. *Intrinsic probabilities of stationary states.* The equality of the intensities of the first and fifth components indicates that the intrinsic probability, or weight, is $m + \frac{1}{2}$, where m is the rotational quantum number. This expression conflicts with the theory of the specific heat of hydrogen, but gives a partial *explanation of the low specific heat of CO at 92° K.* The existence of a band component corresponding to the jump from $m = 1$ to $m = 0$ shows independently that the weight of the state $m = 0$ cannot be zero as in the hydrogen specific heat theory.

41. The luminescence of incandescent titanium oxide. E. L. NICHOLS, Cornell University.—In this oxide the free oxygen present determines the character of the light emitted, and between red heat and 1200° C striking changes in the color of incandescence (red to blue and vice versa) can be produced by a slight adjustment of the oxy-hydrogen flame used in heating. There are two distinct phases: (1) Phase R (oxygen meager) is distinguished by an outcropping of luminescence with a maximum at 950° C which affects the whole visible spectrum. At 950° the red (.65 μ) was 11.5 times and the blue (.45 μ) 9.8 times as bright as the corresponding regions in the spectrum of a black body. (2) Phase O (oxygen in excess) is a modified "blue glow." At 700° the brightness in the blue (.45 μ) was found to be 150 times that of a black body, the green (.52 μ) 48 times, and the red (.65 μ) 8 times. The effect differs from the normal blue glow in that the maximum of relative intensity lies within the incandescent range and the luminescence extends to the green and red of the spectrum. Above 1200° C all excess radiation disappears and the spectrum coincides with that of a black body both in distribution and brightness.

42. Phosphorescence caused by active nitrogen. E. P. LEWIS, University of California.—In 1904 the writer first described the spectrum of the afterglow of active nitrogen, in the Astrophysical Journal, and showed that mercury and other metallic vapors in the discharge tube participated in it. Recently he has found that some solid compounds phosphoresce in the presence of active nitrogen drawn from the discharge tube. The light is green and the spectrum continuous except in the case of the first two substances named below, which show characteristic bands. Strong effect: Uranium nitrate, uranium-ammonium fluoride, ZnS, $BaCl_2$, $SrCl_2$, $CaCl_2$, CsCl. Weak: LiCl, NaCl, KCl, NaI, KI, Na_2CO_3, $SrBr_2$. No effect: K_2SO_4, KNO_3, KOH, HgBr, $CaCO_3$, $CaSO_4$, CaS, $PbCl_2$, CdI_2, $MgNO_3$, $ZnCl_2$, $MnCl_2$, ThO, chalk, sugar, and sulphate of quinine. It is remarkable that light-sensitive CaS is not affected. None of the substances were chemically pure. Excepting the first three, the active substances are not excited by light, but are by cathode rays. With the same exceptions, the effect is produced only after partial drying, but not after complete calcination. The presence of free electrons in the active nitrogen, which may be responsible for its properties, is indicated by the fact that when it streams past an insulated electrode, positive electricity is discharged but not negative, showing much greater mobility for the positive ions.

43. The velocities of emission of photo-electrons in the normal and selective photo-

electric effects. HERBERT E. IVES, A. T. and T. and Western Electric Research Laboratories.—If a polished plate of platinum is placed at the center of an evacuated bulb whose walls are covered with metallic potassium, the plate becomes covered with a thin layer of potassium which preserves the surface configuration of its support, and which is highly photo-electric. Upon illuminating the plate by light polarized in and at right angles to the plane of polarization, it is possible to study to great advantage the characteristics of the normal and selective photo-electric effects. Voltage-current curves made on such a cell show that the stopping potential for the selective effect is larger by a fraction of a volt than for the normal effect. When the plate is slightly warmed, the whole cell being in liquid air, the voltage-current curves for illumination by light polarized in different planes become the same. This is in harmony with a previous observation that the selective effect is destroyed in a thin film of this character in the initial stages of evaporation of the film.

44. Duration of light emission by hydrogen canal rays. A. J. DEMPSTER, University of Chicago.—Canal rays were allowed to pass through a small hole in the cathode into a second chamber at a very much lower pressure. With certain discharge conditions the rays ceased to be luminous in $1\frac{1}{2}$ to 4 cm; with others a strong continuous bundle masked the dying-out phenomenon. By measuring the dependence of the intensity of the bundle on the pressure of the gas in the high vacuum chamber and simultaneously observing the Doppler effect, it was found that the continuous bundle is not due to residual luminosity, but to a second type of long-lived sources carried in from the discharge tube, whose radiation process lasts longer than 6×10^{-7} seconds. A strong electric field was found to have no effect either on the long-lived or short-lived rays. The dependence of intensity on pressure shows that no rays are present that die out completely in a much shorter time than 10^{-7} seconds. The explanation proposed is that the short-lived particles are neutral hydrogen atoms, and that the continuous bundle is due to the dissociation of neutral molecules. The classical radiation theory and Bohr's theory are discussed in connection with the above observations and with those of the Stark effect in a variable electric field.

45. Intensity relations in the helium spectrum. A. LL. HUGHES and P. LOWE, Queen's University.—The intensity distribution in the helium spectrum was investigated as a function of the energy of impact of the electron on the atom. Electrons were accelerated in a three-electrode tube from a filament through a nearby grid into a field-free space. Spectra of the light from this space were photographed for different accelerating voltages (34 to 210). Intensities were measured by a micro-photometer and also by the neutral gray wedge method. The energy distribution curve for any line was found to be characteristic of the series to which it belongs. The singlet series (parhelium) are strongest at high voltages, while the doublet series (orthohelium) are strongest at low voltages. The $1S - mP$ curves rise very rapidly from 34 to about 80 volts, beyond which there is little change. The $1P - mD$ curves show a definite maximum at about 60 volts. The $1P - mS$ curves are approximately constant after a small initial rise. The doublet series curves all drop rapidly from 34 volts onwards, the steepness being least for the $1\pi - m\delta$ series. The enhanced line $\lambda 4686$ appeared above 85 volts and was fairly strong at 210 volts, when some Pickering series lines were faintly visible.

46. Some new photoelectrical and thermoelectrical properties of molybdenite. W. W. COBLENTZ, Bureau of Standards.—Continuing the investigation of molybdenite, MoS_2 reported upon in previous communications (Bur. Stds. Tech. News. Bull. No. 61, May 11th, 1922; Jour. Wash. Acad. Sci. 12, p. 411, 1922), it is found that when there is a close coincidence of the loci of maximum thermoelectrical and photoelectrical sensitivity, the thermoelectrical reaction seems to function like a valve, which amplifies or weakens the photoelectrical reaction, depending upon the direction of the impressed battery current through the crystal. From previous experience, the photoelectric current should be found to be proportional to, but independent of, the direction of the

"dark" battery current through the crystal. In the present instance the photoelectric current is amplified or weakened, according as the external battery current flows with or against the thermoelectric current. As a result of this selective action, instead of obtaining the same photoelectrical reaction (the same galvanometer deflection, after correcting for any difference that may exist in the "dark" conductivity) on reversal of the battery current, there is an outstanding difference (1.5 to 2.5 times) between the maximum and the minimum photoelectrical effect. This is true of both positive and negative maxima of thermal e.m.f.'s.

47. Photoelectric effect of cæsium vapor and a new determination of Planck's universal constant h. JAKOB KUNZ and E. H. WILLIAMS, University of Illinois.—The ionization potential V_I is related to the convergence frequency ν_I of the principal series in the spectrum of the vapor by the expression $V_I e = h\nu_I$ where h is Planck's universal constant and e the charge of the electron. In view of the results in the x-ray region, we may expect an interchangeability in the effect of electron collision and radiation, *i.e.*, we may expect a gas to be ionized whether it is struck by an electron moving with the critical velocity corresponding to V_I or illuminated by radiation of the corresponding wave-length. To test this cæsium vapor was illuminated by ultra-violet light. The result was that for light below a certain wave-length, about 318 m μ, ionization was produced, whereas above this value no effect could be detected. Substituting in the above equation the frequency corresponding to this wave-length and the known values of V_I and e, we obtain for h the value $6.58 \cdot 10^{-27}$, while the accepted value is $6.554 \cdot 10$ erg sec.

48. The transfer of radiation momentum in quanta. WILLIAM DUANE, Harvard University.—According to the idea that radiation carries with it momentum as well as energy, whenever a ray changes its direction it changes its momentum also. If the law of the conservation of momentum applies to such changes, the transfer of momentum must take place between the radiation and matter. The fundamental assumption is now made that a transfer of momentum of this kind takes place in quanta, each of which is proportional to the action constant h. Dimensional reasoning suggests that a quantum equals a whole number multiplied by h and divided by a distance. The theory explains the normal reflection of x-rays by a crystal, including the reflection of rays characteristic of the chemical elements in the crystal (discovered by Dr. Clark and the author) according to the usual law. The paper includes applications of the theory to ordinary light in which equations are deduced for a number of problems of interference and diffraction. The distance to be used is the length characteristic of the apparatus in the direction considered. In general an equation derived from the principle of interference may be transformed into one representing the difference between two radiation momenta as equal to nh divided by a distance.

49. Wave-length measurements of scattered x-rays. ARTHUR H. COMPTON, Washington University.—X-rays from a tube with water-cooled, molybdenum target are scattered by graphite at different angles, and the spectrum of the scattered x-rays has been investigated. It is found that a single line in the primary beam is broken up into two or more lines in the scattered beam. If λ_0 is the wave-length of the primary beam, the shortest line in the scattered beam is λ_0, and the longest is $\lambda_0 + \delta\lambda$, where $\delta\lambda = (1 - \cos\theta)h/mc$, h, m and c having their usual significance. Thus $\delta\lambda = .0242(1 - \cos\theta)$ in Ångströms. When the x-rays are scattered by the graphite at 135°, there may be a third line between these two extremes.

The quantum theory, proposed by the writer to account for the change in wave-length of x-rays due to scattering, suggests that the longest line is scattered by very loosely bound electrons which are free to recoil from the momentum of the scattered x-ray quantum, while the line of unchanged wave-length is scattered by electrons held too firmly to recoil in this manner. Any intermediate lines on this view are due to electrons which recoil only after losing an appreciable amount of energy. It may thus be possible to distinguish the scattering by the different groups of electrons within the atom.

50. Precision measurements of the crystal structures of Al_2O_3, Fe_2O_3 and Cr_2O_3. WHEELER P. DAVEY, General Electric Research Laboratory.—These crystals all have rhombohedral lattices. Using the methods of x-ray crystal analysis previously described the following results were obtained:

Crystal	Side of unit triangle	Axial ratio	Density from x-ray data	Density from literature
Al_2O_3	4.745 A	2.726	4.001	3.99
Fe_2O_3	5.035 A	2.726	5.243	5.19–5.30
Cr_2O_3	4.932 A	2.754	5.256	5.215

In all three crystals there are three molecules per unit prism. This gives the structure of diamond, except that the cube is stretched along its body-diagonal. The high axial ratio can be explained by assuming a hexahedral molecule consisting of an equilateral triangle of oxygen with a metal atom immediately above and below the center of the triangle. Such a structure was early predicted by Bragg. These oxides are therefore "valence compounds," and should not be decomposed by an electric field while in the molten state. The small residual fields would account for the stability of these oxides at high temperatures.

51. The crystal structure of aluminum carbide, determined without the use of x-rays. M. L. HUGGINS, Harvard University.—The general tendencies operative in crystal formation have been determined from a study of the positions of valence electrons in crystals whose atomic arrangements are known. A knowledge of these tendencies, of the empirical formulæ, the number of valence electrons in each case, usually the crystal symmetry, and sometimes other crystallographic data, is sufficient to determine the most probable structures of many crystals. These can often be checked up by means of comparisons of interatomic distances or by the data on crystal symmetry, axial ratios, cleavage, twinning, rotation of polarized light, the crystal faces observed, etc., so that the structures are as definitely determined as if deduced from x-ray measurements. The structure of Al_4C_3, determined in this way, with no other information than that the substance forms yellow, rhombohedral crystals of density 2.36, which are stable in a vacuum up to 1400°, is one in which each Al atom is surrounded by 3 C atoms and each C by four Al atoms, all at tetrahedron corners. The average Al-C distance is about 2.02 A. It is predicted that c/a will be found to be about 1.225, and that the (0001) faces will be found to be polar.

52. The effect of x-rays on halite and sylvite. P. L. BAYLEY, Cornell University.—Many chemical compounds are visibly colored by x-rays. Halite turns a dark brownish yellow and becomes colorless after several days of exposure to bright daylight. Sylvite turns a deep purple which fades entirely after a few minutes of exposure to daylight. The author has examined the rate of fading and the absorption of these materials as functions of the wave-length. Halite has a very broad absorption band at the edge of the violet which extends far into the ultra-violet and the visible green. Sylvite has a broad absorption band in the yellow and green. As both substances fade, the peaks of their absorption curves do not change position. The fading of sylvite follows the same absorption-time curve regardless of the intensity of the color produced by exposures to x-rays for different lengths of time. These curves show roughly that the amount of the fading is proportional to the depth of the color. Halite fades most rapidly when exposed to the bluish green part of the spectrum and sylvite most rapidly when exposed to the orange. Because of the difference in the colors produced in this way, a short exposure to x-rays makes possible the easy separation of the two materials as they occur naturally in the Stassfurt mines in masses of crystals of both kinds.

53. An experiment with mercury vapor. M. SCOTT, Cornell University.—The striking potential of an arc in mercury vapor has been shown to depend upon the electron density (Yao, Phys. Rev. **21**, p. 1, 1923) and the vapor density (Scott, Phys. Rev. **21**, p. 204, 1923). K. T. Compton and Y. T. Yao (Compton, Phys. Rev. **20**, p. 296, 1922)

have recently drawn the conclusion that the striking potential depends upon the distance from the liquid surface to the ionization chamber. The explanation offered is that the mercury atom changes from one metastable state to another during its travel away from the liquid surface. In a series of experiments, the writer has investigated this, and finds that the striking potential does depend upon the distance of the ionization chamber from the liquid surface so long as condensation of the vapor is allowed in any part of the system but that this dependence disappears when condensation is stopped. The effect is due, then, not to a change in state of the atom but to a change in vapor pressure, a result previously reported by the writer.

54. On terminal speeds and mobilities of electrons in gases. K. T. COMPTON, Princeton University.—When electrons move in a gas under the influence of an electric field, they acquire kinetic energy from the field and from the thermal energy of the molecules, and lose energy as the result of momentum imparted to molecules at impacts. They tend to acquire a steady average terminal speed. A study is made of the magnitude of this speed under various conditions, of the rate at which this speed is acquired and of the total number of collisions made while advancing a given distance. This terminal speed, when substituted into a well-known expression for mobility, gives an equation which differs nowhere by more than 12 per cent from that derived by Loeb by the more approximate method suggested by Townsend (Loeb, Phys. Rev. **19**, p. 24, 1922). The more important results are: $f = 2(m/M)(1 - \Omega/U)$; $U_t = \Omega/2 + (\Omega^2/4 + f^2 ME^2/4.536m)^{\frac{1}{2}}$; $u = 0.815le/[me\Omega + 2me(\Omega^2/4 + W^2)^{\frac{1}{2}}]^{\frac{1}{2}}$, where f is the average fraction of energy lost at a collision, m and M are the masses of electron and molecule, eU and $e\Omega$ are their average kinetic energies, eU_t is the terminal energy of electrons in field E, l is their mean free path and eW is the energy which they would acquire from the field if the molecules were at rest.

55. Ionization potentials of He, Hg, H_2, N_2, O_2, NH_3, H_2O. C. A. MACKAY,[1] Princeton University.—The ionization potentials of these gases were investigated by a method, originally suggested by Hughes (Hughes and Dixon, Phys. Rev. **10**, p. 496, 1917), by which effects due to radiation may be almost entirely suppressed. Photoelectrons were used to produce ionization, since a hot filament would dissociate some of the gases investigated. Corrections due to initial velocities and contact potential differences were made by comparing each gas with one whose critical potential is known, as follows: The ionization potential of mercury was taken as the standard, its value being 10.4 volts. Helium and mercury vapor were mixed, and discontinuities in the current-voltage curve found at the ionization potentials of both gases, so that the true value for helium was determined by comparison with that for mercury. Then helium was mixed with each of the other gases and their ionization potentials determined with reference to it. The following values were obtained for He, H_2, N_2, O_2, NH_3 and H_2O respectively: 24.5, 15.8, 16.3, 12.6, 11.1, and 13.2 volts. No additional ionization potentials were detected in the range up to 50 volts, but such critical potentials would have been masked by the effect of the lower potentials, unless strong. It is noted that the value for helium agrees with Lyman's spectroscopic series limit, but that the value for oxygen is much lower than that given by Foote and Mohler.

56. The radiotron as a source of negative electric resistance. OTTO STUHLMAN and D. A. WELLS, University of North Carolina.—In place of a tube specially designed for the purpose as used by Hull (I. R. E. 6, 1918), a radiotron of the 201 U. V. type may be used to produce similar results. The filament is heated in the usual way. A constant difference of potential with the positive terminal connected to the plate is maintained between the grid and plate. In series with these is placed the variable positive resistance. A variable source of electromotive force, with its negative terminal connected to the negative terminal of the filament, is inserted between it and the negative terminal of the plate battery. Under these circumstances the current flowing through the positive resistance depends on the velocity of impact of the primary thermions on the grid and

[1] Introduced by K. T. Compton.

on the number of secondary electrons leaving the grid and moving towards the plate. The net current flowing through the resistance is then the difference between the number of primary electrons that strike and enter the grid and the number of secondary electrons which leave it. When the number of secondary electrons becomes larger than the number of primary, all the characteristic voltage-current relations shown by Hull in his paper are obtained.

57. Stages in the excitation of the thallium spectrum. F. L. MOHLER and A. E. RUARK, Bureau of Standards.—Photographs of the spectra of thallium excited by low voltage thermionic discharge, and electrical measurements of ionization, inelastic impact and radiation give results consistent with the configuration assigned by Bohr to the three valence electrons. The normal orbit of the outermost electron is $2p_2$ with an energy of 6.1 volts. The transition $2p_2$ to $2p_1$ gives an inelastic collision without radiation at 1.0 volt. At 3.3 and 4.5 volts we have true resonance potentials resulting in the emission of the first lines of the sharp and diffuse series respectively. Another line spectrum appears near 12 volts. This is evidently a second arc spectrum resulting from the removal of one of the two more firmly bound valence electrons.

58. Some experiments on the polarization capacity of electrolytes. IRVING WOLFF, Cornell University.—*Variation of polarization capacity with frequency.* Using an impedance bridge, with a three-stage vacuum tube amplifier in the detecting circuit, measurements were taken at frequencies from 200 to 6000 per second. A modification of this bridge with a heterodyne and vacuum tube as detector was used for frequencies from 10,000 to 100,000 per second. The measurements taken on platinum and gold electrode cells in sulphuric acid show an increasing rate of change of capacity with higher frequency. The opposite effect is predicted by the theories. *Effect of superposing two different frequency sine currents on a cell.* Two vacuum tube oscillating circuits were set up and their outputs coupled simultaneously to the bridge. The cell was found to have a different measured capacity with each of the frequencies. Furthermore, the resistance and capacity, measured with either frequency, was found to be independent of whether the other was present, even when the latter had by far the greater intensity. This result is predicted by the concentration change theory, but could not be explained by the theory which considers the capacity caused by the condenser action of a thin gas film at the electrode.

59. Demonstration of the variable character of the vowel ē. G. W. STEWART, University of Iowa.—Professor D. C. Miller's analysis of the sustained vowel ē as in *meet* indicates two important resonance regions surrounding the frequencies 308 and 3100. That the vowel did not have the same character throughout was evident from his curves. The purpose of the present demonstration is to exhibit to an audience this changing character and something as to its nature. Syllables containing the vowel are spoken through an acoustic filter cutting off above 3000 and then through one cutting off above 2400. The vowel in *eat* cannot be recognized in either case, whereas the vowel in *meet* can be recognized in both cases, in the former better than in the latter. This recognition depends upon the frequencies existing when passing from the consonant to the sustained vowel. The frequency region below 3000 must be prominent in this transition state. The changing character may be explained by the enlargement of the orifice into the mouth cavity and the consequent raising in pitch of the resonance frequencies. The demonstration suggests analogous considerations in regard to all vowel sounds and calls attention to the importance of the nature of the preceding consonant in the recognition of vowel sounds. It points out the need for a complete investigation of vowel sounds.

60. Physics of lubrication, II. Viscosity under pressure. MAYO D. HERSEY, U. S. Bureau of Mines, and HENRY SHORE, Massachusetts Institute of Technology.—Viscosities of five typical lubricating oils (two fixed oils and three mineral oils) are given up to 4000 kg/cm² and at temperatures from about 20° to 100° C, and are represented by empirical equations. Plasticity or apparent solidification occurs at various pressures

from 1200 kg/cm² upwards depending on the oil and its temperature. At moderate pressures and temperatures the effect of pressure is more pronounced on the mineral than on the fixed oils, but this order of sequence changes at higher pressures and temperatures. A rolling ball viscosimeter was used and calibrated by means of liquids of known viscosity and density. The work was begun at Harvard University and makes use of methods for high pressure measurement due to Prof. P. W. Bridgman.

61. An x-ray examination of ZnO in vulcanized rubber. WHEELER P. DAVEY, General Electric Research Laboratory.—The method was that previously described for the precision measurement of crystals (Phys. Rev. May, 1922). Preliminary experiments showed that gum rubber contained no crystalline substance. Two samples of vulcanized rubber containing ZnO were tested. In both cases a diffraction pattern was obtained which was identical to within 0.1 per cent with the pattern of ordinary ZnO. There was no evidence of crystalline sulphur or of ZnS.

62. Note on Liouville's theorem. W. F. G. SWANN, University of Minnesota.—The density τ of a group of points in a $2n$-dimensional space varies with the time according to the law $D\tau/Dt + \tau\Sigma^n(\partial p_s/\partial p_s + \partial \dot{q}_s/\partial q_s) = 0$ where the q's and p's represent coördinates in the space. When q_s and p_s refer to corresponding coördinates and momenta in a system obeying the Hamiltonian equations, the quantity in brackets vanishes, and $D\tau/Dt = 0$. The energy of the waves in the perfectly reflecting box discussed in radiation theory may be written in the form $E = \Sigma\, p_s^2/4a_s + \Sigma\, b_s q_s^2$. Now a strict interpretation of the statistical theory pertaining to the radiation problem requires that there shall be many coördinates of each kind, alike in the sense of their contributions to the energy being expressed as the same function of the coördinates. By choosing new quantities P_s and Q_s defined by $P_s = p_s/(4a_s)^{\frac{1}{2}}$, and $Q_s = q_s(b_s)^{\frac{1}{2}}_s$ we can secure a condition in which all terms contribute to E in the same form, but the quantities P_s and Q_s are no longer related by the Hamiltonian equations. It turns out, however, that the equations which they do satisfy lead to $(\partial \dot{P}_s/\partial P_s + \partial \dot{Q}_s/\partial Q_s) = 0$ so that they may be taken as coördinates for the representation of the system in a $2n$-dimensional space with the assurance that the relation $D\tau/Dt = 0$ will hold for them.

63. Duration of the 4.9-volt resonance radiation in mercury vapor. HAROLD W. WEBB, Columbia University.—A modification of the method described at the February meeting for measuring the duration of radiation produced by electronic impact, was used. The results there given were the average value for a mixture of radiation. The ordinary four-electrode tube, consisting of a filament, first grid, second grid, and photoelectric plate, was filled with mercury vapor at 35° C. A.C. voltages, in phase, were applied to the two grids, that on the first grid having maximum and minimum values with respect to the filament of 4.4 and 5.2 volts respectively, so that only the 4.86 volt radiation ($\lambda = 2537$), with some 4.68 volt radiation as shown by the D.C. characteristics, was present. The photoelectric currents with increasing frequencies were measured. These began to decrease at 200 cycles, and at 1500 cycles were practically equal to that found for continuous radiation. Assuming the radiation to decay exponentially, the exponential constant was measured as 4000. The results point to a metastable state in the mercury vapor similar to that found by Kannenstine in helium. The effect on the result of the 4.68 volt radiation present has not been determined; a long-lived radiation might be expected from this type of excitation.

64. The crystal structures of some tetragonal crystals. M. L. HUGGINS, Harvard University.—By methods previously outlined, the structures of a number of tetragonal crystals have been determined. In anatase (TiO_2) the Ti atoms are as determined by means of x-rays by Vegard. Each Ti is surrounded by four equidistant O atoms and each O by two equidistant Ti atoms, all at tetrahedron corners. This is also true in rutile (TiO_2). The structure obtained for this substance differs somewhat from those deduced by Vegard and Williams from x-ray data, although in full agreement with that data. Like rutile are SnO_2, PbO_2, MnO_2, MoO_2, RuO_2, $ZrSiO_4$, $ThSiO_4$, YPO_2, and MgF_2. ZrO_2 and SiO_2 (christobalite) probably also possess structures similar to anatase

or rutile. Mn_3O_4 has one of two structures, in both of which each Mn is surrounded by four O atoms and each O by three Mn atoms, at tetrahedron corners. The available data are insufficient to decide between several structures for Mn_2O_3. In $CaWO_4$ the arrangement of the Ca and W atoms has been determined by Dickinson. The oxygens are so situated that each is surrounded by two Ca and two W atoms, at tetrahedron corners, each Ca or W being surrounded by eight O atoms. $PbMoO_4$ is similar. Tetragonal HgI_2 may also have a similar structure, but it is more probably like anatase.

65. The Hall effect in silicon-iron alloys. THOMAS C. MACKAY, Carnegie Institute of Technology.—In work reported in the Physical Review of May, 1913, A. W. Smith found that a large increase in the Hall effect was produced by the addition of small amounts of silicon to iron. The writer has extended the range of these observations, using some very pure silicon-iron alloys obtained from the Research Laboratory of the Westinghouse Electric and Manufacturing Co. It was found that the increment in the Hall effect is approximately proportional to the percentage of silicon up to about 5, the rate of increase being much larger than the corresponding rate of increase of electrical resistance with silicon content.

66. The crossed-orbit model of normal helium, its ionization potential and the Lyman series. LUDWIK SILBERSTEIN, Eastman Kodak Company.—This paper proposes and discusses a formula, based on rigorously circular orbits and derived from the ring model. It gives for the ionization potential 24.35 volts, for an inclination of the orbit planes of 120 degrees. For other remarkably related inclinations the same formula gives Lyman's four lines $OS - mP$ and also Lyman's line 600.5 or $OS - 1S$.

67. The absorption of hydrogen in potassium vapor arcs. ROGERS D. RUSK,[1] University of Chicago.—It has been noted by Gehlhoff and others that hydrogen is rapidly absorbed in hot potassium vapor when subjected to a high tension electrical discharge. In the present experiment potassium was made the anode of a two-electrode tube, and ionization currents were obtained between a coated filament and the anode, through potassium vapor and hydrogen. Absorption was readily obtained with currents of a few milliamperes. In one instance, with a temperature of 190° C and with 80 volts across the arc and 5 milliamperes flowing, the pressure in a volume of 150 cc dropped from .03 mm to less than .0004 mm in four minutes. Arcs could be struck with as low as 6 volts, and it was found that the rate of absorption of hydrogen could be controlled by varying the voltage. At from 6 to 8 volts no absorption occurred in a bright green arc. At about 12 volts absorption appeared, and at 16 volts became quite marked. The arc was then a violet color, showing distinct hydrogen lines, and indicating that the absorption sets in at a potential corresponding to a particular type of ionization of the hydrogen. Acknowledgment is due Dr. A. J. Dempster for suggesting the problem and giving his aid in the work.

68. The positive ions from hot platinum. HENRY A. ERIKSON, University of Minnesota.—The positive ions emitted by hot platinum have been analyzed by means of the method described in the Physical Review, 20, p. 118, August, 1922. It is found that when the mobility of the positive ion from hot platinum in air is measured immediately after formation it is the same as the mobility of the normal negative ion in air or as the normal initial positive ion formed in air by means of the alpha rays from polonium. During an interval of the order of 0.30 of a second, the initial positive ion changes over into the normal positive ion of mobility 1.36 cm/sec/volt/cm. Since in the initial stage, and in the final stage as well, the mobilities are the same as for the positive ion produced in air by the alpha rays from polonium, the conclusion is that the ions are identical, the ions in both cases being produced in air. If the platinum is at a very high temperature and the ions are allowed to remain for a short time in the air which has left the platinum surface, they load up and form heavier positive ions.

69. The mobility of negative ions in air. LEONARD B. LOEB, National Research Fel-

[1] Introduced by A. J. Dempster.

lowship, University of Chicago.—In measuring the mobility of negative ions, using the Rutherford alternating current method, the ions are generated by two methods, (1) by ultra-violet light on one of the plates of the ion chamber; (2) in an auxiliary chamber by alpha particles or ultra-violet light, the ions being driven through the gauze forming one of the plates by a weak auxiliary field. The mobility measured by the first method is 2.1 cm/sec; by the second, with the auxiliary fields generally used, about 1.8 cm/sec. If this discrepancy were due to a change in the ion with time, on increasing the auxiliary field the mobility of the negative ion should change from 1.8 to 2.1, *i.e.*, by a factor of 1.195. Changing this field from about 1.1 to 39.5 volts/cm changes the mobility by a factor of 1.275. The effect of the gauze is therefore not an aging effect, but is probably due to a change in the distance of the average ion from the gauze at the beginning of the negative phase of the auxiliary field. This is borne out by the recent work of Swann and Miss Zimmerschied on the penetration of electrical fields through gauzes (see abstract 71 below). The results obtained using the auxiliary chamber are therefore meaningless. The true value of the mobility is that obtained by the first method, viz., 2.15 ± .05 cm/sec.

70. X-ray absorption coefficients of cobalt and nickel. F. K. RICHTMYER and F. W. WARBURTON, Cornell University.—The mass absorption coefficient of substances for x-rays has previously been shown to obey the law $\mu/\rho = K\lambda^3 + \sigma/\rho$, where for each substance K is a constant which from one element to another varies as the cube of the atomic number. The inversion of the order of atomic weights and atomic numbers in nickel and cobalt makes it of interest to determine K for these two substances. Pure nickel is easily obtained in sheet form. Pure cobalt was finally obtained (by Mr. C. J. Kayko at the General Electric Research Laboratory) by pressing cobalt oxide into a thin placque and reducing in a hydrogen furnace. Between .1 A and .3 A the mass absorption coefficients are given by the equations:

$$\text{For cobalt } (N = 27): \mu/\rho = 124\lambda^3 + .17$$
$$\text{For nickel } (N = 28): \mu/\rho = 144\lambda^3 + .20$$

The constant K is therefore a function of atomic number, rather than of atomic weight as is to be expected from other x-ray phenomena.

71. The passage of ions through a grid under the influence of an electric field. CHARLOTTE ZIMMERSCHIED,[1] University of Minnesota.—If two plates A and C are placed one on each side of, and parallel to, a plane piece of gauze B, the surface of A being a source of ionizing radiations (covered with polonium, for example), a difference of potential between A and B will cause ions to flow through the grid to C, even when C is at the same potential as B, or, as a matter of fact, at a potential slightly nearer to that of A than is the potential of B. A grid is frequently utilized in this way in measurements of ionic mobilities; as in the Frank and Hertz method. Since, in these measurements, it is assumed that the grid acts as though it were a source of ions, whose motion between the plates B and C is entirely determined by the potential difference between them, a careful consideration of the mechanism becomes desirable. Theory shows that the ratio of the number of ions which reach C to the number which reach B and C together should be just equal to the ratio of the number of tubes of force which pass from A to C to the number which start off from the polonium-covered surface of A. This relation has been experimentally verified for a variety of conditions as regards the fields between plates A and B, and B and C.

72. Further results on the diurnal variation of the potential gradient of atmospheric electricity from observations aboard the Carnegie, and comparisons between land and ocean results. S. J. MAUCHLY, Department of Terrestrial Magnetism, Washington, D. C.—Results obtained by the author in 1921 (Phys. Rev. **18**, pp. 161 and 477, 1921), from observations by various observers aboard the *Carnegie*, indicated that the chief

[1] Introduced by W. F. G. Swann.

component of the diurnal variation of the potential gradient consists of a "wave" of 24-hour period whose phase at any given instant is roughly constant over all oceans. Later observations aboard the *Carnegie* have increased the ocean data by about 30 per cent and confirmed the foregoing conclusions. Harmonic analyses of all the data show only a small annual variation in the phase angle of the 24-hour wave. Harmonic analyses of the potential-gradient data from many widely distributed land stations indicate, with few exceptions, a sufficiently close agreement among themselves and with the ocean results to warrant the conclusion that the phase of the 24-hour wave of the diurnal variation at a given instant may, as a first approximation, be looked upon as roughly constant over the whole earth when due account is taken of the extent to which the results of harmonic analysis may reflect local meteorological, topographical, and cultural conditions. The only local-time component of the diurnal variation indicated by analysis of the ocean data is a 6-hour wave which appears to be in general agreement with a similar effect found by L. A. Bauer (Terr. Mag. **27**, p. 28, 1922) in his analysis of the potential gradient at Tortosa.

CORRECTION

Free and forced heat convection in gases and liquids. CHESTER W. RICE, General Electric Research Laboratory, p. 474, April, 1923. Instead of $W_c = KA(k/\nu)v\Delta t_{\text{avg.}}$, read: $W_c = KA(v/\nu)k_{\text{avg.}}\Delta t$.

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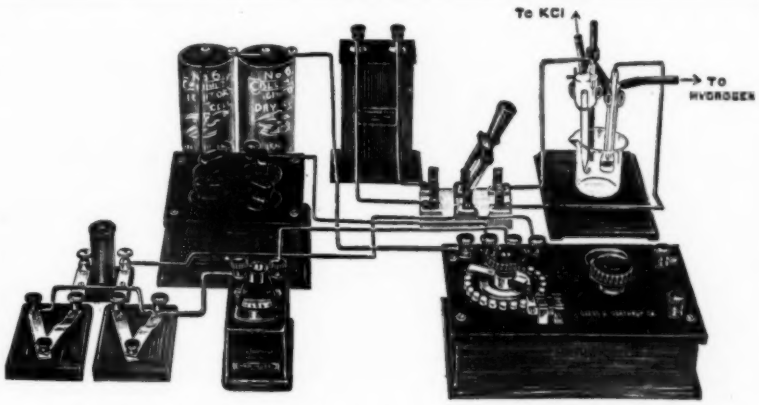

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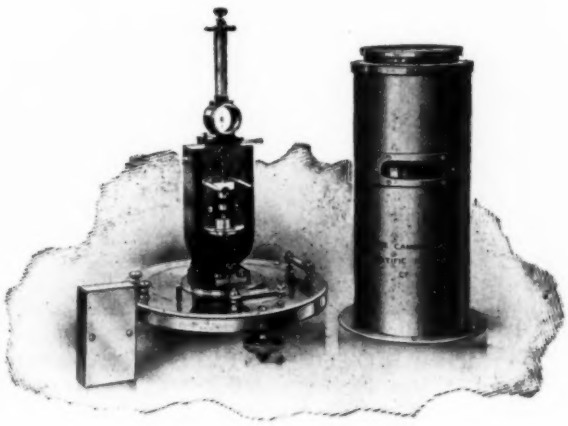

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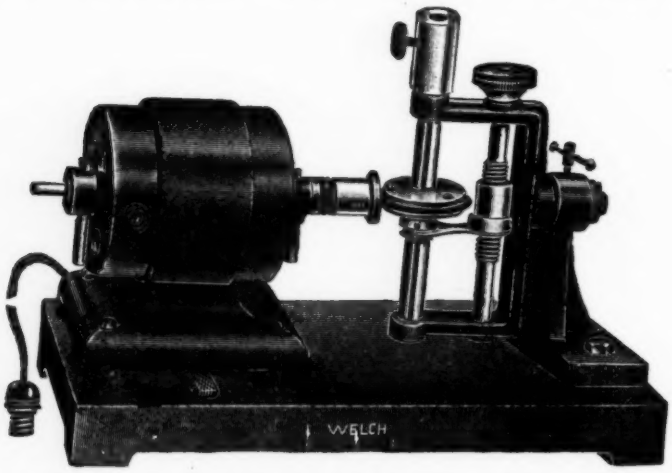

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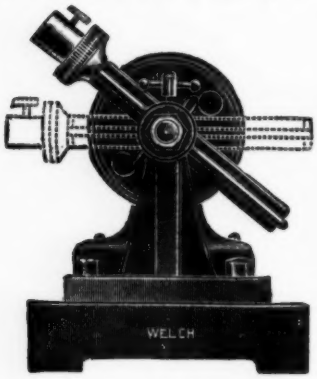

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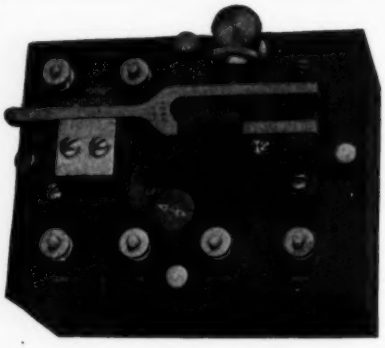
2. *Subtitles.*—Write, first, a title describing the group of results forming the main contribution of the article, including all that belong together. If there are in addition results which do not come under that title, gather them into as few groups as possible and formulate a complete and precise title for each group. For examples of such subtitles see the italicized parts of the abstracts in current numbers of the REVIEW. The subtitles should together form a complete index of the new information. They should be formulated before the text is written.

3. *Text.*—Write a paragraph adequately summarizing the main group of results and including the corresponding subtitles, and then do likewise for the other groups. A separate paragraph should be used for each distinct subject involved, but all material which can easily be grouped together under a single title should be summarized in the same paragraph. Parts of subtitles may be scattered through the text, but the subject of each paragraph must be given at the beginning. Italicize subtitles but no other words or phrases.

4. *Final Checking.*—Re-read the article so as to check the abstract, and correct any omissions and mistakes; read the subtitles by themselves to see that they properly index the information; and read the abstract to see whether it cannot be condensed and its English be improved. The abstract should be made as readable as the necessary brevity will permit.



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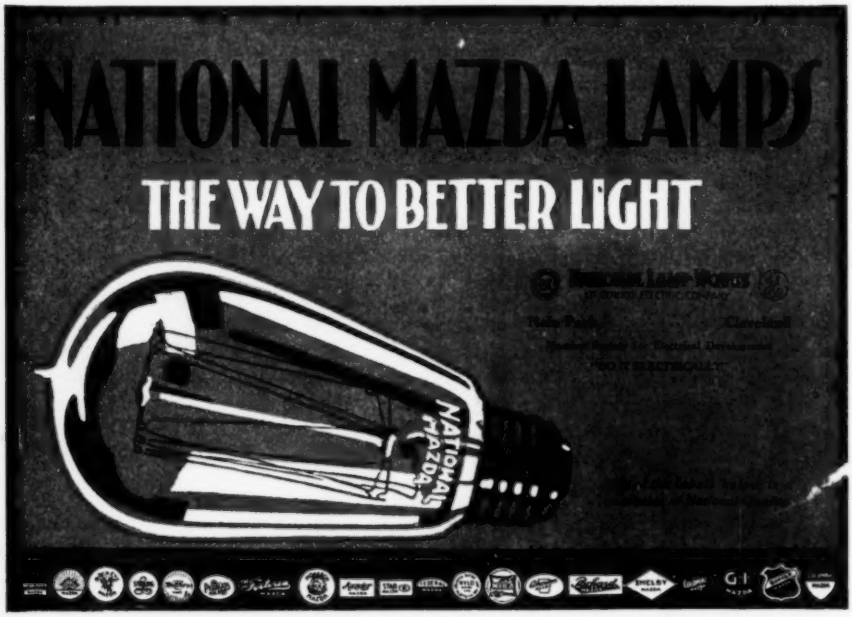

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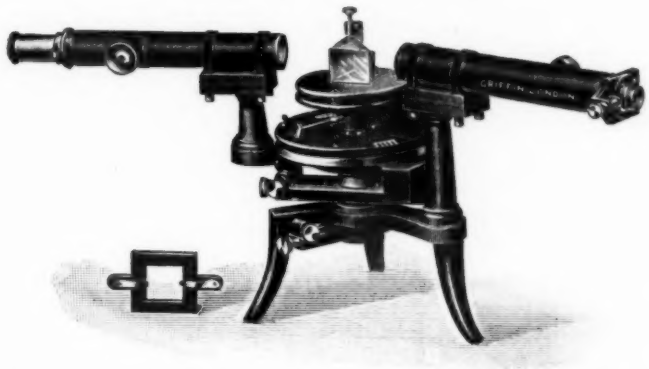

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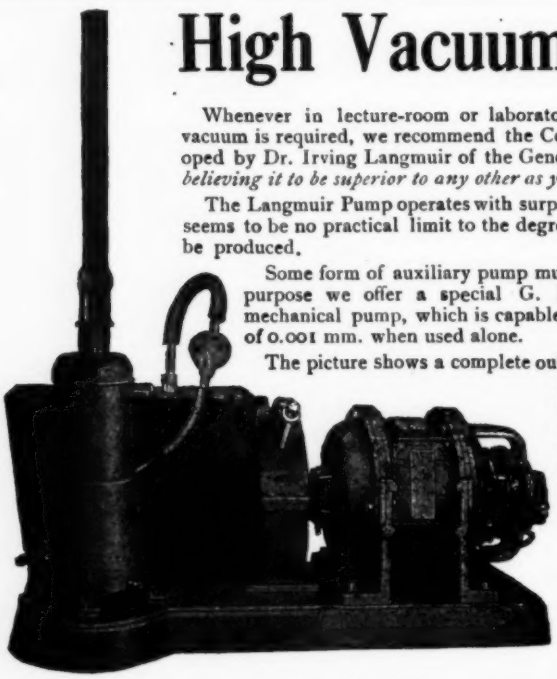

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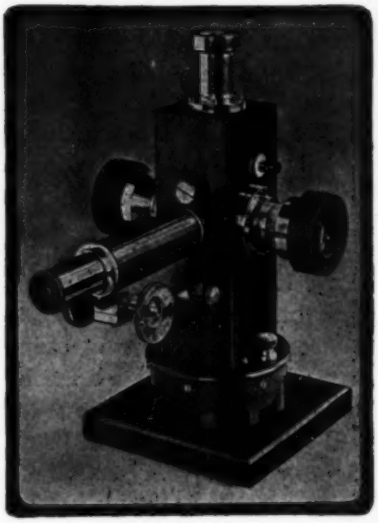

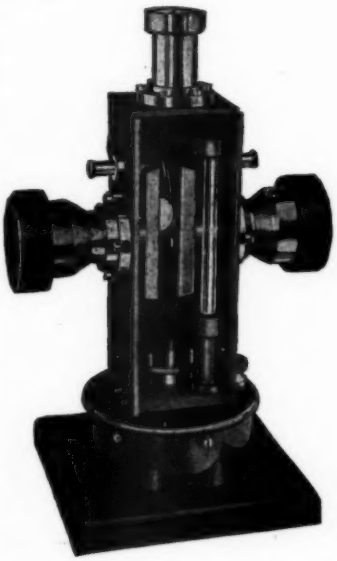

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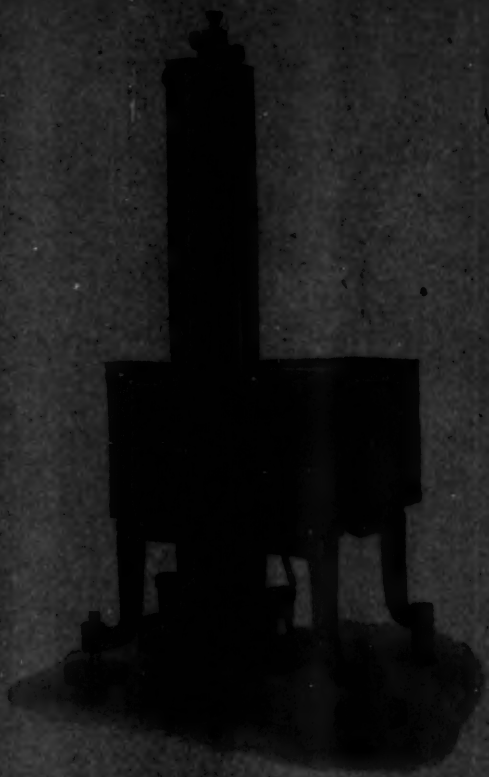

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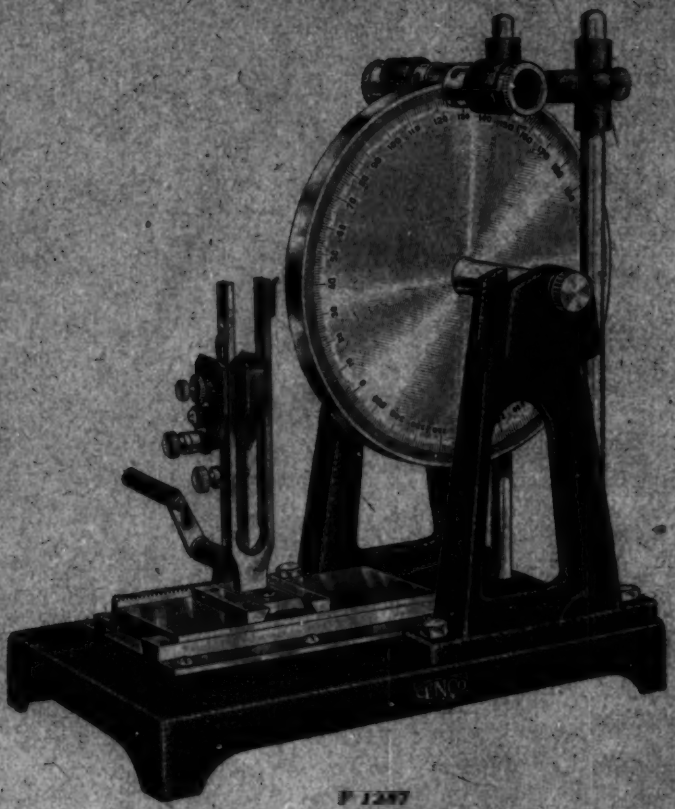

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